August 2004 • NREL/SR-510-36392

Subcontractor Report

Kinetic and Modeling Investigation to Provide Design Guidelines for the NREL Dilute-Acid Process Aimed at Total Hydrolysis/Fractionation of Lignocellulosic Biomass

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Model Development

The kinetic pattern of dilute-acid hydrolysis of lignocellulosic materials and the conceptual sketch of counter-current reactor are shown in Figure 1. The countercurrent reactor is simply a continuous flow reactor in which the directions of liquid and solid are reversed. The shrinking-bed operation in the countercurrent reactor induces continual reduction of solid velocity moving through the reactor. Hemicellulose and cellulose exhibit the biphasic kinetic behavior upon acid hydrolysis. In Fig.1, the fast-hydrolyzed fraction of hemicellulose is represented by H_1, and the slow-hydrolyzed fraction as H_2. The two hemicelluloses are first hydrolyzed to form soluble oligomers, then the oligomers are converted to xylose and decomposed products. However, in the case of cellulose, the hydrolysis of cellulose is often modeled simply as two consecutive reactions as shown in Fig. 1. This is because, the amorphous cellulose which is taken to be the fast-hydrolyzed portion, proceeds extremely fast and also no oligomeric concentration is generally detected. A universal model is developed which is applicable to both hemicellulose and cellulose hydrolysis and also for shrinking and non-shrinking bed operation by appropriate adjustment of process parameters. An important feature of this new model is that axial dispersion (or back mixing) is considered in **the liquid flow**.

Mathematical Modeling

Previous investigations indicate that the acid hydrolysis of lignocellulosic biomass can be modeled as first-order reactions. The rate constant, k_i, is then represented by the Arrhenius equation in which the acid concentration term, S, is absorbed into the pre-exponential factor.

$$k_i = k_{io} S^{ni} e^{-E_i / RT} \tag{1}$$

A mathematical model for the dilute-acid hydrolysis of hemicellulose is first developed as follows. The following assumptions are made in this modeling: (1) axial dispersion (or backmixing) **for solid flow** is negligible; (2) the reaction and physical conditions (temperature, acid concentration, porosity, solid bulk density, and bed voidage) are uniform within the reactor; (3) the internal and external mass transfer effects are negligible.

Because the first order nature and the isothermal condition, the hemicellulose hydrolysis kinetic pattern shown in Figure 1 can be simplified into unbranched reaction sequence:

$$H \xrightarrow{K_H} O \xrightarrow{k_3} X \xrightarrow{k_4} D$$

Where $K_H = F*k_1 + (1-F)*k_2$, and F is the fraction of easily hydrolyzable hemicellulose.

An overall solid material balance and a material balance for hemicellulose (H) within a differential segment of the reactor under steady state give the following differential equations.

$$\rho(1-\varepsilon)\frac{dv}{dx} - fK_H C_H = 0 \tag{2}$$

$$\frac{d(vC_H)}{dx} - K_H C_H = 0 \tag{3}$$

With the boundary conditions of:

$$x = L, \quad v = v_O$$
$$x = L, \quad C_H = C_{HO}$$

Where ε is the bed voidage; ρ is the bulk density of feedstock; and f is the ratio of total mass solubilized over hemicellulose solubilized during the hydrolysis. The factor, f, is an entity greater than one since components other than hemicellulose are also dissolved during the process including lignin, extraneous components, and small fraction of cellulose. The hemicellulose

content in the solid (C_H) is defined on the basis of the reactor volume. It is notable that v (the solid linear velocity) is treated as a variable (not a constant) in the bed shrinking model. One would expect that v decreases as the solid moves through the reactor, the effect of shrinking.

From Equations 2 and 3, the following single equation is obtained.

$$v\frac{dC_H}{dx} + [fk_H / \rho(1-\varepsilon)]C_H^2 - k_H C_H = 0 \tag{4}$$

With the boundary condition of:

$$x = L, \quad C_H = C_{HO}$$

From the material balance for oligomer (O) and xylose (X) in the liquid stream, the following additional set of differential equations is obtained.

$$D\frac{d^2C_O}{dx^2} - u\frac{dC_O}{dx} + k_1(C_H / \varepsilon) - k_3C_O = 0 \tag{5}$$

$$D\frac{d^2C_X}{dx^2} - u\frac{dC_X}{dx} + k_3C_O - k_4C_X = 0 \tag{6}$$

With the boundary conditions of:

$$x = 0, \quad C_O = 0$$
$$x = 0, \quad C_X = 0$$
$$x = L, \quad \frac{dC_O}{dx} = 0$$
$$x = L, \quad \frac{dC_X}{dx} = 0$$

The concentration terms, C_O and C_X, are defined on the basis of liquid volume.

In dimensionless form, Equations (4)-(6) are expressed as:

$$\frac{dY_H}{dZ} + \frac{\beta\omega}{q}[\,(Y_H^2 / \lambda) - Y_H\,] = 0 \tag{7}$$

$$(1/Pe)\frac{d^2Y_O}{dZ^2} - \frac{dY_O}{dZ} + (\beta / \varepsilon)Y_H - \beta\alpha_3 Y_O = 0 \tag{8}$$

$$(1/Pe)\frac{d^2Y_X}{dZ^2} - \frac{dY_X}{dZ} + \beta\alpha_3 Y_O - \beta\alpha_4 Y_X = 0 \tag{9}$$

where $q = v/v_O$, $\beta = k_H L/u$, $\omega = u/v_O$, $\lambda = (1-\varepsilon)\rho/(C_{HO}f)$, $Z = x/L$, $Y_H = C_H/C_{HO}$,

$Y_O = C_O/C_{HO}$, $Y_X = C_x/C_{HO}$, $Pe = Lu/D$, $\alpha_3 = k_3/k_H$, $\alpha_4 = k_4/k_H$

With boundary conditions of:

$$Z = 1, \quad Y_H = 1$$
$$Z = 0, \quad Y_O = 0$$
$$Z = 1, \quad \frac{dY_O}{dZ} = 0$$
$$Z = 0, \quad Y_X = 0$$
$$Z = 1, \quad \frac{dY_X}{dZ} = 0$$

The initial hemicellulose concentration in the solid feedstock is defined as

$$C_{HO} = H_O(1-\varepsilon)\rho v_O$$

Where H_O is the initial hemicellulose content in untreated biomass. The yield is defined as

$$\text{Yield} = \frac{\text{(xlose + oligomer) recovered in liquid}}{\text{Total hemicellulose content in solid feedstock}} = \frac{\varepsilon u(C_O + C_X)}{v_O C_{HO}} = \varepsilon\omega(Y_O + Y_X)$$

Shrinking Factor, q

A shrinking factor (q) is defined as the ratio of solid linear velocity (v) at any point in the reactor to that at the reactor entrance point (v_O). It is an entity that is less than one since bed shrinking reduces the solid linear velocity. An explicit solution can be obtained for the shrinking factor from Equations (2) and (3). In the process one needs to express dv/dx term explicitly on the left had side in Equation (2) and likewise for $d(vC_{H0})/dx$ in Equation (3) and dividing one equation by the other. The resulting equation is then integrated to obtain the solution for q as

expressed by Equation (10). It is seen that the shrinking factor is a function of hemicellulose composition in solid (Y_H) only since λ is a constant ($\lambda = \rho/fC_{HO}$).

$$q = \frac{v}{v_O} = \frac{\lambda - 1}{\lambda - Y_H} \tag{10}$$

Equation 7 can be simplified using Equation 10 to give the following

$$\frac{dY_H}{dZ} - \frac{\beta\omega}{\lambda(\lambda - 1)}[Y_H^3 - 2\lambda Y_H^2 + \lambda^2 Y_H] = 0 \tag{11}$$

Equations 8, 9 and 11 will be solved simultaneously with aforementioned boundary conditions and using kinetic parameters selected from previous investigations (Table 1). The important process variables such as solid feeding velocity, linear liquid velocity, temperature, bed shrinking, and sulfuric acid concentration will be studied. Sugar concentration, yield and reactor processing capacity are output parameters which will be used to assess reactor performance.

An important feature of the model for hemicellulose is that it is also applicable to cellulose hydrolysis as well as the non-shrinking bed operation with the adjustment of process parameters. For example, with the assumption of $k_1 = k_2 = k_C$ and $k_3 = k_G$, $k_4 = 0$ the hemicellulose kinetic pattern is simplified into two consecutive first-order reactions which represents the pattern for the cellulose hydrolysis. The conversion of the model from hemicellulose into cellulose becomes complete with adjustment of the kinetic parameters (E_i, k_{io}, and n_{io}). Furthermore, if one arbitrarily take the f value to be very small, then λ value becomes very large and q value approaches 1 indicating no changes in solid velocity. The model under this special case then becomes a non-shrinking one.

Dispersion Model Simulation Results and Discussion

Yellow Poplar Sawdust was selected as the substrate in this study. On dry basis, it was analyzed to contain 19.63% XMG [xylose (15.48)+mannose(3.08)+galactose(1.08)], 47.98% glucan, 22.33% K. lignin, and 10.06% others. Based on our discussion with NREL, regarding very dilute-acid hydrolysis on yellow poplar, it was assumed that 50% of the lignin and others were also solubilized along with hemicellulose. Therefore the f value is calculated to be 1.82 during the stage of hemicellulose hydrolysis. After the hemicellulose fraction is completely solubilized, the remaining solid is calculated to contain 85% glucan and a total of 15% lignin and other materials. It was also assumed that 50% of lignin and others are solubilized along with cellulose hydrolysis. The value of f is therefore calculated to be 1.09 in the subsequent cellulose hydrolysis.

The kinetic parameters used in this study are selected from previous investigations (Table 1). The following known and estimated process parameters are introduced for the simulation.

(1) About 6 g of substrate can be packed in a 30 mL reactor which gives $\rho^*(1-\epsilon) = 0.2$ and it was assumed constant throughout regardless of the solubilization of hemicellulose and cellulose (our lab data)

(2) The fraction of fast-hydrolyzed portion of the total hemicellulose of yellow poplar (F) is 0.70. (our previous investigation)

(3) The length of the reactor is 6" (actual size of our laboratory reactor).

(4) Peclet number, a measure of axial backmixing was assumed equal to 20.

The important process variables studied in this work are the solid feeding velocity, linear liquid velocity, temperature, bed shrinking, and sulfuric acid concentration. Sugar concentration, yields, and high reactor processing capacities are the output parameters considered in connection with the reactor performance.

Effect of Initial Solid Feeding Rate

The effect of the initial solid feeding rate was investigated at 190°C with 0.08 wt% sulfuric acid and the liquid linear velocity of 2.0 cm/min. The initial solid feeding rate is an index for the reactor processing capacity. The basic reaction conditions are selected from previous investigations. As shown in Figure 2 the hemicellulose content in solid and solid linear velocity are the function of the initial solid feeding rate (v_O) and the reactor position (Z). The shape of the hemicellulose profiles indicates that the solid feeding rate (v_O) is an important factor affecting the reactor performance and thus needs to be optimized. Taking the profile of hemicellulose where v_O = 5.0 cm/min in Fig.2, it is clear that the conversion is too low, achieving only 53.3% at the solid exit point (Z=0). Taking the other extreme where v_O = 0.5 cm/min, the hydrolysis reaction is now overly done as the conversion is essentially complete where Z = 0.56, or within the first 44% of the reactor path (note that Z=1 at the solid entering point). The optimum of v_0 ($V_{o,\ opt}$) does exist. The true optimum can only be determined from an economic model accounting the yield, product concentration and processing capacity among other things. In this work we take a simplistic approach by setting an arbitrary criterion that v_0 reaches optimum when the conversion for hemicellulose at the solid exit point (Z=0) is 0.995 or Y_A = 0.5%. Under the given set of conditions, the optimum initial solid feeding rate is found to be 1.09 cm/min. At a rate lower than this, the hydrolysis of hemicellulose is finished far before the outlet point causing excessive

decomposition. At a rate higher than the optimum, the hydrolysis of hemicellulose is incomplete leaving much of the hemicellulose unreacted when the solid leaves the reactor.

It is also seen in Figure 2 that both hemciellulose content in solid and the solid linear velocity decline rather abruptly then level off along the direction of solid feeding. With v_o = 1.09 cm/min, 90% of original hemicellulose is hydrolyzed when the solid is at the half way point in the reactor (Z=0.5). This means that the major fraction of sugar is produced in vicinity of the solid inlet point and it has relatively a small distance to travel before being washed out the reactor. It is the primary feature of the countercurrent reactor that minimizes the residence time for sugar degradation thus raising the yield and sugar concentration. This feature is further enhanced in the shrinking-bed operation. In this mode, the solid moving velocity slows down as the reaction proceeds. The solid with unhydrolyzed hemicellulose stays even to the liquid outlet point.

The modeling results are similar for cellulose hydrolysis (Figure 3). The optimum initial solid feeding rate was determined to be 0.6 cm/min for the reaction conditions selected in this study. The results of the simulation confirm that the benefit of the shrinking bed operation also applies to the cellulose hydrolysis. Figure 3 shows the profile of remaining cellulose (the extent of the bed shrinkage) across the reactor position. The extent of bed shrinkage reached as high as 92%. Since the solid amount in the reactor is reduced, the liquid throughput can be reduced also to retain same level of concentration and yield. In this situation, we project that the acid solution can be reduced by about 50% in comparison to the non-shrinking bed operation.

Effect of Temperature

The temperatures and acid concentration are two main factors controlling the hydrolysis reactions especially in terms of substrate conversion and sugar decomposition. Reaction temperature applied for hydrolysis of biomass has been in the range of 160 -210°C for the hemicellulose and 210-250°C for cellulose. With the countercurrent shrinking bed reactor, the exposure time of sugar to high temperature is reduced thus limiting its decomposition. This in turn allows the reaction to be conducted at high temperatures. The sulfuric acid concentration used in the simulation is the same as that applied in recent NREL investigation, i.e., 0.08 wt%. It is much lower than those used in studies prior to recent NREL work. The simulation results shown in the Figure 4 indicate that the sugar yields for hemicellulose can reach 99% when the temperature is below 190°C, and decrease slightly when the temperature is above 200°C. The overall yield declines about 6% as the temperature is raised from 160°C to 210°C. Obviously the yield of hemicellulose sugars is rather insensitive to the temperature at the acid concentration of 0.08 wt%. The reactor processing capacity and the product concentration, however, are very sensitive to the change of temperature. The simulation results also indicate that the oligomers are the predominant product at all temperatures, however, monomeric xylose concentration increases at a faster rate than that of the oligomeric concentration as the temperature is raised from 160°C to 210 °C.

The effect of temperature on cellulose hydrolysis is summarized in Figure 5. Unlike hemicellulose, yield of glucose is strongly affected by temperature. The glucose yield is seen to decrease from 96% to 68% when the temperature is raised by 40°C from 210°C. Similar to the hemicellulose hydrolysis, the reactor processing capacity and glucose concentration sharply increase with temperature. It may be noted that although the yield decreases sharply at high temperatures for a given liquid velocity, it is possible to improve the yield even at high

temperature by increasing the liquid flow rate. This effect of liquid velocity is shown later in the text.

Effect of Acid Concentration

The effect of acid concentration on the hydrolysis of hemicellulose and is summarized in Figure 6 respectively. As seen in Figure 6, the acid concentration has similar effect as that of the temperature on the hemicellulose hydrolysis. That is, the maximum reactor processing capacity can be increased with slight reduction in yield as the concentration of acid is increased from 0.06 to 0.30 wt%. Again it should be emphasized here that the slightly lower yield obtained at higher acid concentration at a given flow rate can be further improved, provided a lower concentration than that shown in the figure 6 is acceptable. This process of increasing the yield at the expense of product concentration is shown later in the text. Both xylose concentration and the reactor processing capacity increase linearly with the acid concentrations. The oligomer concentration in liquid stream increases slightly initially and then levels off to a near constant value of 2.4 g/100ml.

We were unable to study the effect of acid concentration on cellulose hydrolysis due to the limitation of our kinetic parameter shown in table 1. The kinetic parameter for cellulose hydrolysis was estimated using only one acid concentration.

Although the effect of acid concentration is similar to the effect of temperature (increased reactor processing capacity and thereby increased sugar concentration), we recommend the use of temperature as the process variable for process adjustments. It is desirable to keep the acid concentration low primarily because one need not worry about recovering it and also low acid levels would generate less waste sludge and reduced disposal problems.

Effect of Acid Flow Rate

The effects of liquid flow rate on the acid hydrolysis of hemicellulose were studied with 0.08 wt% sulfuric acid. The simulations were conducted under the selected temperatures at 170°C, 190°C, and 210°C and its consequent $V_{o,\ opt}$. The $V_{o,\ opt}$ is determined as shown in Figure 2 for the given temperature and acid concentration. As the liquid flow rate increases, one expects (1) an increase in sugar yield, since the degradation of sugars is reduced as the sugars experience a shorter residence time inside the reactor and (2) a decrease in sugar concentration because of more liquid input. Figure 7 shows that the liquid linear velocity has no effect on the yield at the relatively low temperature such as 170°C. This is because the yield has already reached its maximum (close to 100% of theoretical). The sugar concentration (xylose+oligomer) at this temperature decreases with the liquid flow rate as expected. As the reaction temperature increases, the liquid flow rate becomes a critical factor governing the sugar yield and sugar concentration. For example, at the temperature of 210°C, the reactor maximum processing capacity was found to be 4.29 cm/min. The sugar yield is increased substantially from 70 to 95% as the liquid flow rate is raised from 1.0 cm/min to 2.5 cm/min. For liquid flow rates beyond 2.5 cm/min, the increase in sugar yield is marginal, but the sugar concentration continuously decreases. From these simulation results, w conclude that the hydrolysis of hemicellulose at 190°C and with 0.08 wt% sulfuric acid and liquid linear velocity of 2.0 cm/min is one set of the practical conditions for yellow poplar in terms of yield (98.5%) and sugar concentration (2.6 g/100mL).

The effects of liquid flow velocity on the cellulose hydrolysis are summarized in Figure 8. At the temperature of 210°C, although the glucose yield is quite high, the sugar stream is

simply too dilute. At 230°C, the glucose yield increases from 70% to 95% as the liquid flow velocity is increased from 1.0 cm/min to 7.0 cm/min. Further increase of the liquid flow velocity did not improve the yield but brought about only the dilution of the sugar product. At 250°C, the glucose yield jumps abruptly from 39.5% to 85% as the liquid flow velocity is increased from 1.0 cm/min to 7.0 cm/min. However, the glucose concentration decreased from 25.1 g/100 mL to 7.6 g/100 mL. From these simulation results, we conclude that the hydrolysis of cellulose at 230°C and with 0.08 wt% sulfuric acid and liquid linear velocity of 5.0 cm/min is one set of the practical conditions for yellow poplar in terms of yield (93%) and sugar concentration (2.4 g/100 mL). The acid flow velocity did not influence the conversion levels in both hemicellulose and cellulose hydrolysis.

Effect of Peclet number

Peclet number is one measure of degree of backmixing in the liquid flow. It is inversely proportional to diffusivity. A higher peclet number indicates lesser backmixing and vice-versa. The effect of peclet number on the acid hydrolysis of hemicellulose (and cellulose) were studied with 0.08 wt% sulfuric acid, temperature of 190°C (230 °C for cellulose) and Vo,opt of 1.09 cm/min (0.6 cm/min for cellulose). Figures 9 and 10 show the simulation results obtained at varying acid flow velocity at different dispersion levels. As the peclet number decreases, one expects a decrease in sugar yield, since the degradation of sugars is increased as the sugars experience a longer residence time inside the reactor due to back mixing. Figures 9 and 10 show that at any given liquid velocity, as the peclet number decreases, sugar yield also decreases. The drop in yield is more pronounced below peclet number of 3. At peclet number = 1, yield obtained was only 53% (41% for cellulose) at a flow velocity of 2 cm/min and any increases in acid flow

velocity brought about only marginal improvement in yield with steady dilution of the product stream. At the same point, yield obtained when peclet number = 10000 was 99% (84% for cellulose). The conversion levels at at all peclet numbers were essentially the same indicating that the drop in yield was purely due to degradation of sugars due to back mixing. At peclet no = 20 (obtained at NREL reactors), the model predicts that the yield for both hemicellulose and cellulose would be only marginally lower than that of the ideal countercurrent reactor (Pe = 10000). Furthermore, at acid velocity beyond 2.0 cm/min, the difference in yield would be practically negligible.

Effect of Bed Shrinking

The advantage of the shrinking-bed operation over the non-shrinking one is brought out well in Figure 11 for both hemicellulose and cellulose hydrolysis. The thin solid lines shown connect the yield and concentration obtained at different liquid velocity under shrinking and non-shrinking bed operation. As shown in Figure 11, at the liquid velocity of 3 cm/min, the yield for cellulose hydrolysis reached as high as 88% under shrinking bed operation while the yield was only 69% under the non-shrinking bed operation. Also, glucose concentration obtained was much lower in the non-shrinking mode than that in the shrinking mode for the identical operating conditions. It may be noted however, that the drop in yield and concentration for cellulose hydrolysis is not entirely due to sugar degradation under non-shrinking mode. The extent of conversion was 99.9% under shrinking while it was only 81% under non-shrinking under identical process conditions. In other words, the optimum solid feeding rate was much lower under non-shrinking than that under shrinking for the same process conditions. At the liquid velocity of 3 cm/min, the maximum solid feeding rate was found to be only 0.17 cm/min under

non-shrinking while it was as high as 0.6 cm/min for shrinking. Even under the reduced solid feeding rate, the yield obtained under non-shrinking is lower than that obtained under shrinking at any given level of sugar concentration. Alternatively, taking a sample point from the simulation results in order to achieve the same cellulose yield of 92% for the given conditions except the solid feeding rate, the glucose concentration is 2.4 g/100ml for the bed-shrinking operation and 1.1 g/100ml for non-shrinking one, 118% increase. Figure 11 also shows that the benefit of bed shrinking applies for the hemicellulose hydrolysis as well. But, the extent of bed shrinkage is much smaller for hemicellulose (35%) than that for cellulose (92%). Consequently, the effect of it is also much smaller for hemicellulose than it is for cellulose.

Notations

C_C	cellulose concentration (g/100 mL)
C_{CO}	initial C_C
C_H	hemicellulose concentration in solid (g/100 mL reactor volume)
C_{HO}	initial C_H
C_O	oligomer concentration (g/100 mL liquid volume)
C_X	xylose concentration (g/100 mL liquid volume)
E_i	activation energy for k_i (kcal/g mol)
f	ratio of solubilized biomass to solubilized hemicellulose (or cellulose), 1.82(1.09)
H	hemicellulose
H_1	fast hydrolyzed hemicellulose
H_2	slow hydrolyzed hemicellulose
H_O	percentage of hemicellulose content in original biomass
k_i	rate constant of hemicellulose hydrolysis (min^{-1}), $k_i = A^{ni}k_{oi}exp(-E_i/RT)$
koi	frequency factor for k_i ($min^{-1}(wt\%)^{-ni}$)
k_C, k_G	rate constant of cellulose hydrolysis (min^{-1})
k_H	rate constant, $k_H= F*k_1 +(1-F)*k_2$
L	reactor length (cm)
n_i	acid concentration exponent
O	hemicellulose oligomer
Pe	Peclet number (= Lu/D)
q	bed shrinking factor, v/v_O
R	universal gas constant
S	acid concentration (wt%)
T	temperature (^OK)
u	liquid linear velocity (cm/min)
v	solid linear velocity (cm/min)
v_O	initial linear solid feeding velocity (cm/min)
X	xylose
Y_H, Y_O, Y_X	C_H/C_{HO}, C_O/C_{HO}, C_X/C_{HO}
Z	x/L

Greek

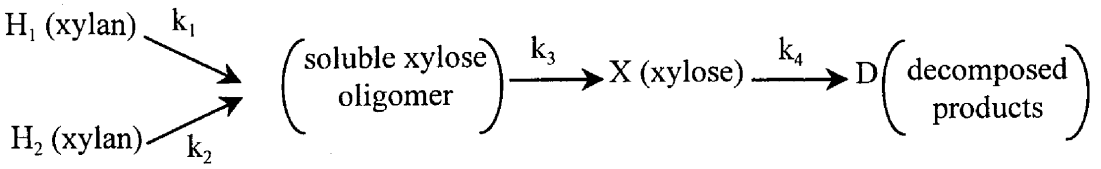
α_3, α_4	k_3/k_H, k_4/k_H
β	k_HL/u
ε	void fraction in bed
λ	$\rho/(fH_O)$
ρ	bulk density
ω	u/v_O

Table 1. Kinetic parameters from previous investigations

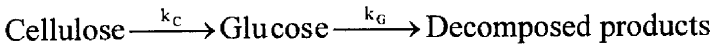
	$k_i = k_{io}(C_A)^{ni}\exp(-E_i/RT)$ for hemicellulose $k_i = k_{io}\exp(-E_i/RT)$ for cellulose			
Hemicellulose[a] (Chen et al, 1996)	k_i	k_{io} $min^{-1}(wt\%)^{-ni}$	n_i	E_i kcal/g mol
	1	1.458×10^{15}	1.0	30.9
	2	1.300×10^{14}	0.5	30.0
	3	6.372×10^{10}	1.5	21.0
	4	1.618×10^{12}	0.8	27.5
Cellulose[b] (Wu et al, 1997)	k_i	k_{io} $min^{-1}(wt\%)$		E_i kcal/g mol
	1	1.4×10^{18}		44.511
	2	1.81×10^{13}		33.215

[a] Kinetic study conducted using Yellow Poplar Sawdust as the substrate at the temperature of 160-190°C and 0.049-0.196 wt% sulfuric acid.

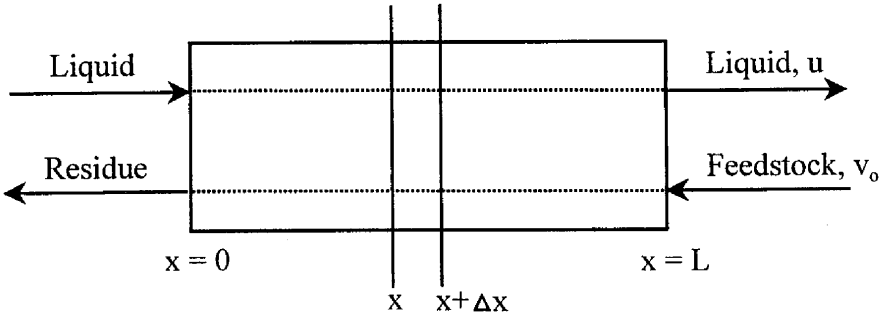
[b] Kinetic study conducted using Yellow Poplar Sawdust as the substrate at temperature of 205-235°C and 0.064 wt% sulfuric acid.



(A) Kinetic pattern of hemicellulose hydrolysis. H_1 refers to the easily hydrolyzed hemicellulose fraction, and H_2 refers to the difficult hydrolyzed portion.



(B) Kinetic pattern of cellulose hydrolysis



(C) Countercurrent reactor

Figure 1. Kinetic pathway of acid hydrolysis of lignocellulosic biomass and conceptual sketch of countercurrent reactor.

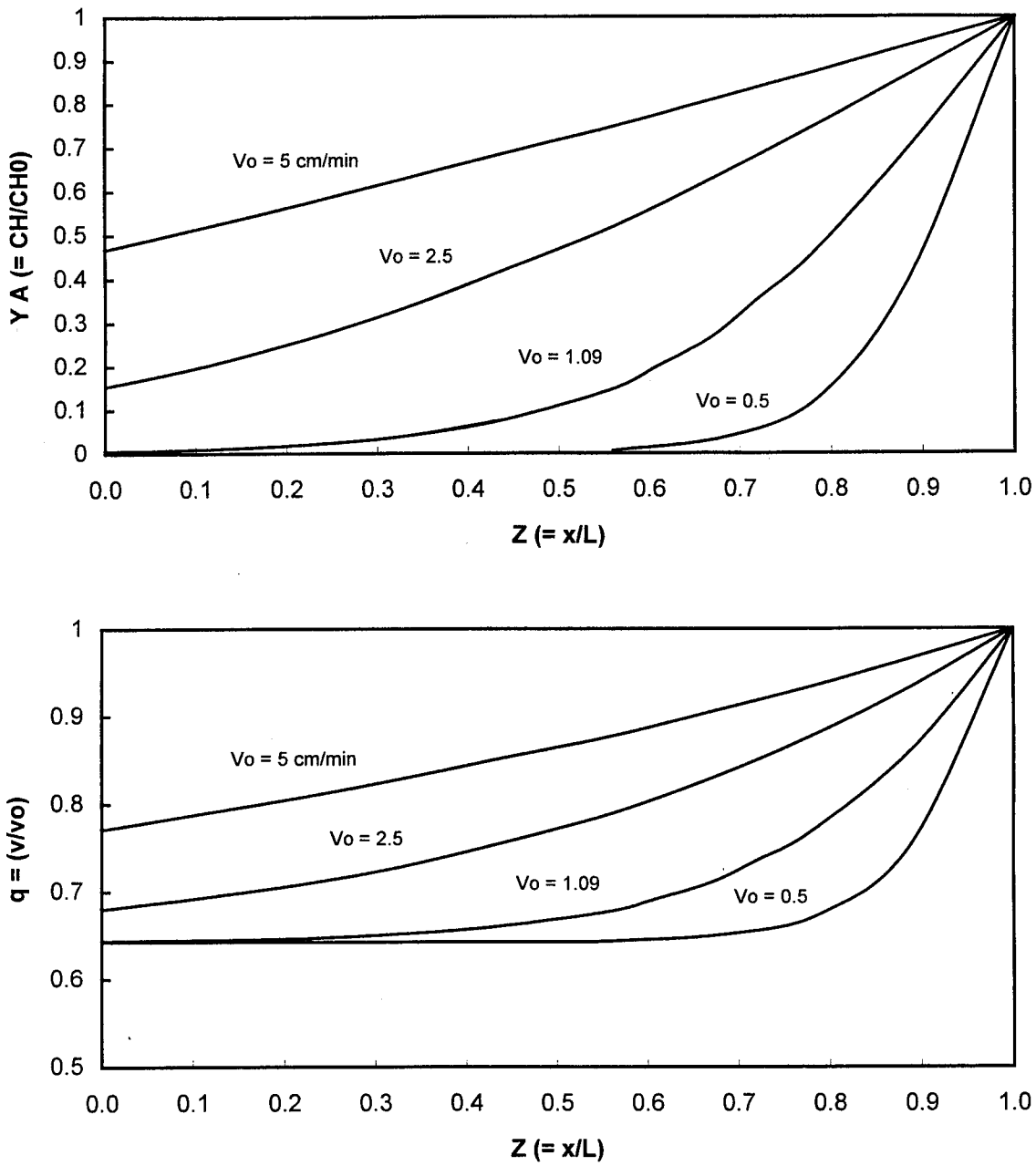


Figure 2. Effect of initial solid feeding rate on the hydrolysis of hemicellulose. Assumption: T = 190 C, u = 2 cm/min, acid concentration = 0.08 wt% sulfuric acid, peclet no = 20.

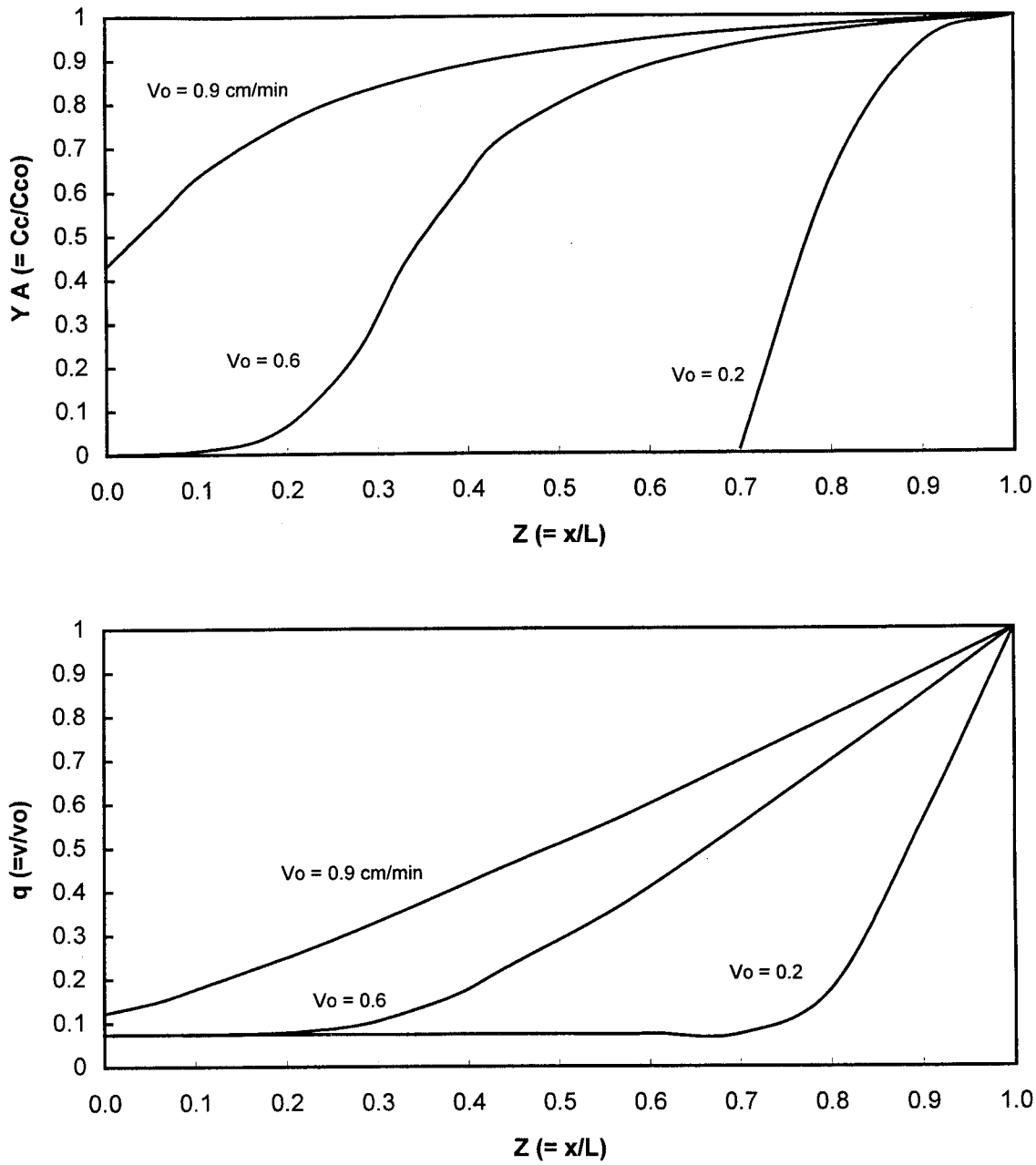
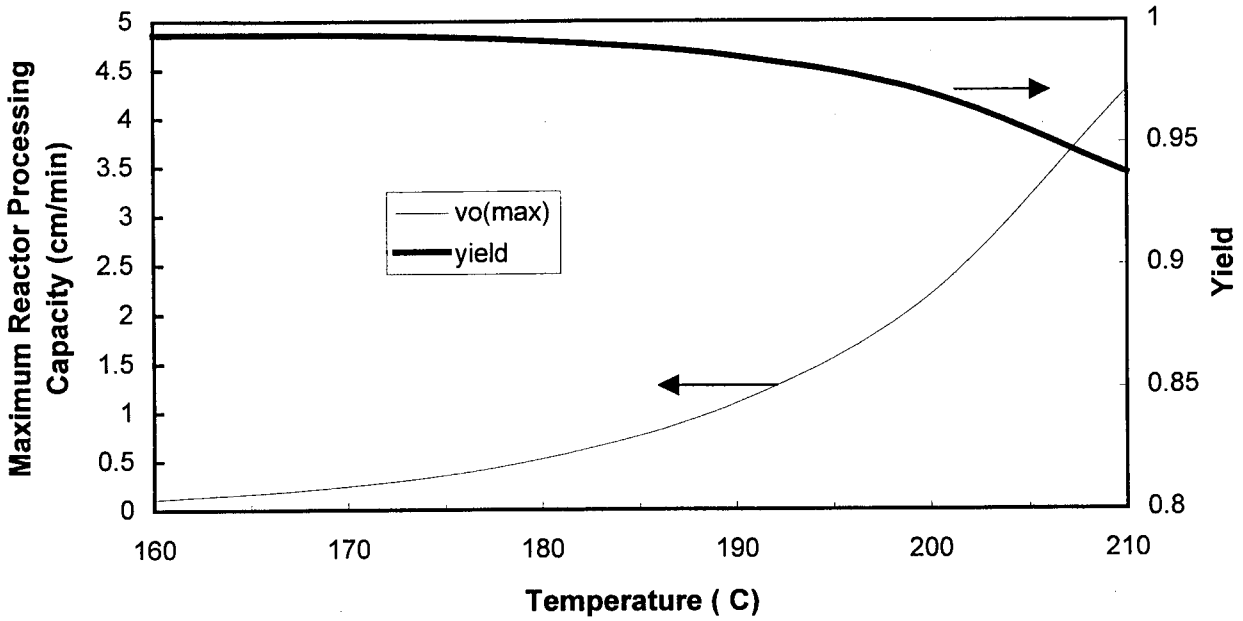


Figure 3. Effect of initial solid feeding rate on the hydrolysis of cellulose. Assumption: T = 230 C, u = 3 cm/min, acid concentration = 0.08 wt% sulfuric acid, peclet no = 20.



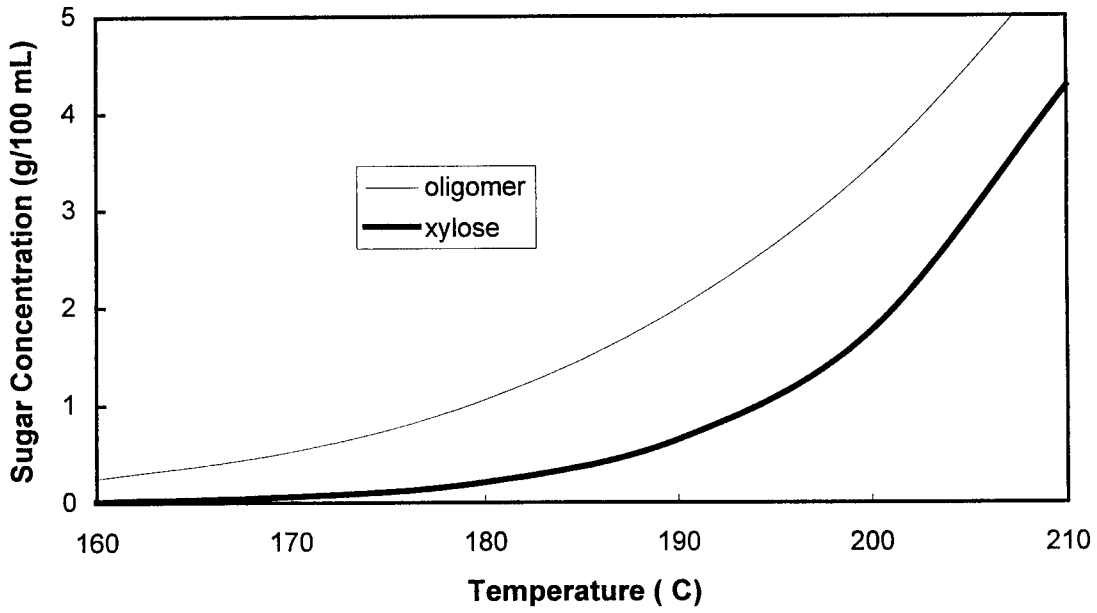
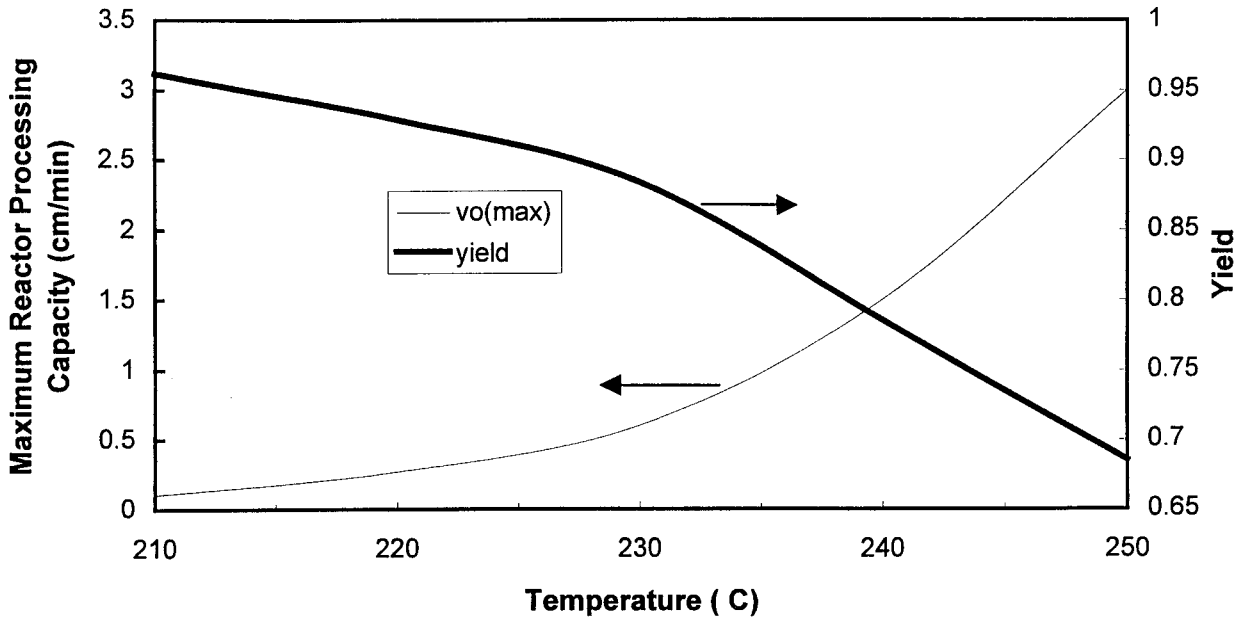


Figure 4. Effect of temperature on the hydrolysis of hemicellulose. Assumption: u = 2 cm/min and acid concentration = 0.08 wt% sulfuric acid, Peclet no = 20.



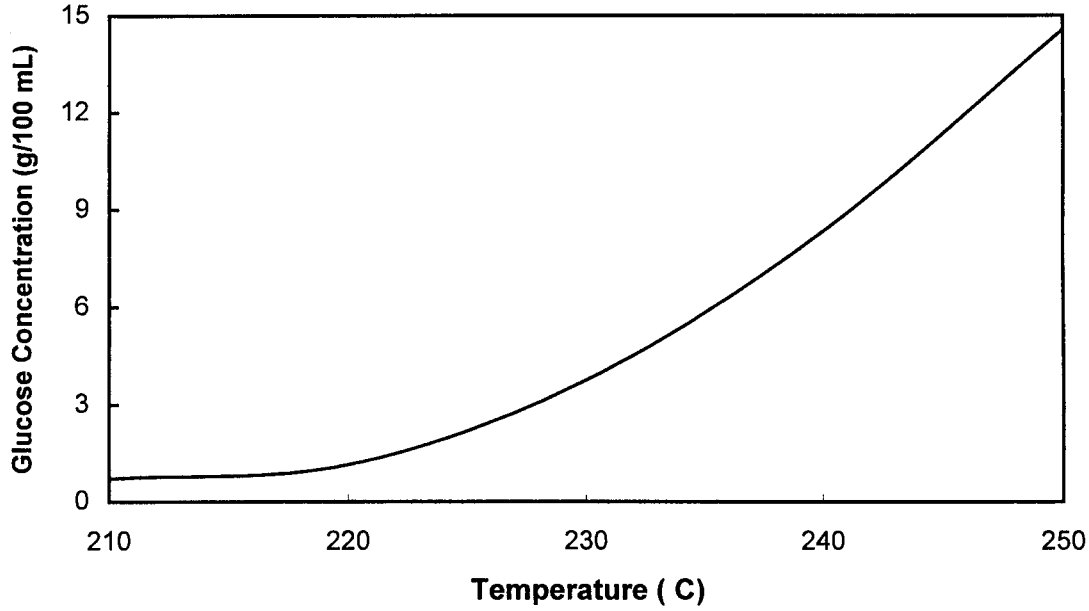


Figure 5. Effect of temperature on the hydrolysis of cellulose. Assumption: u = 3 cm/min and acid concentration = 0.08 wt% sulfuric acid, Peclet no = 20.

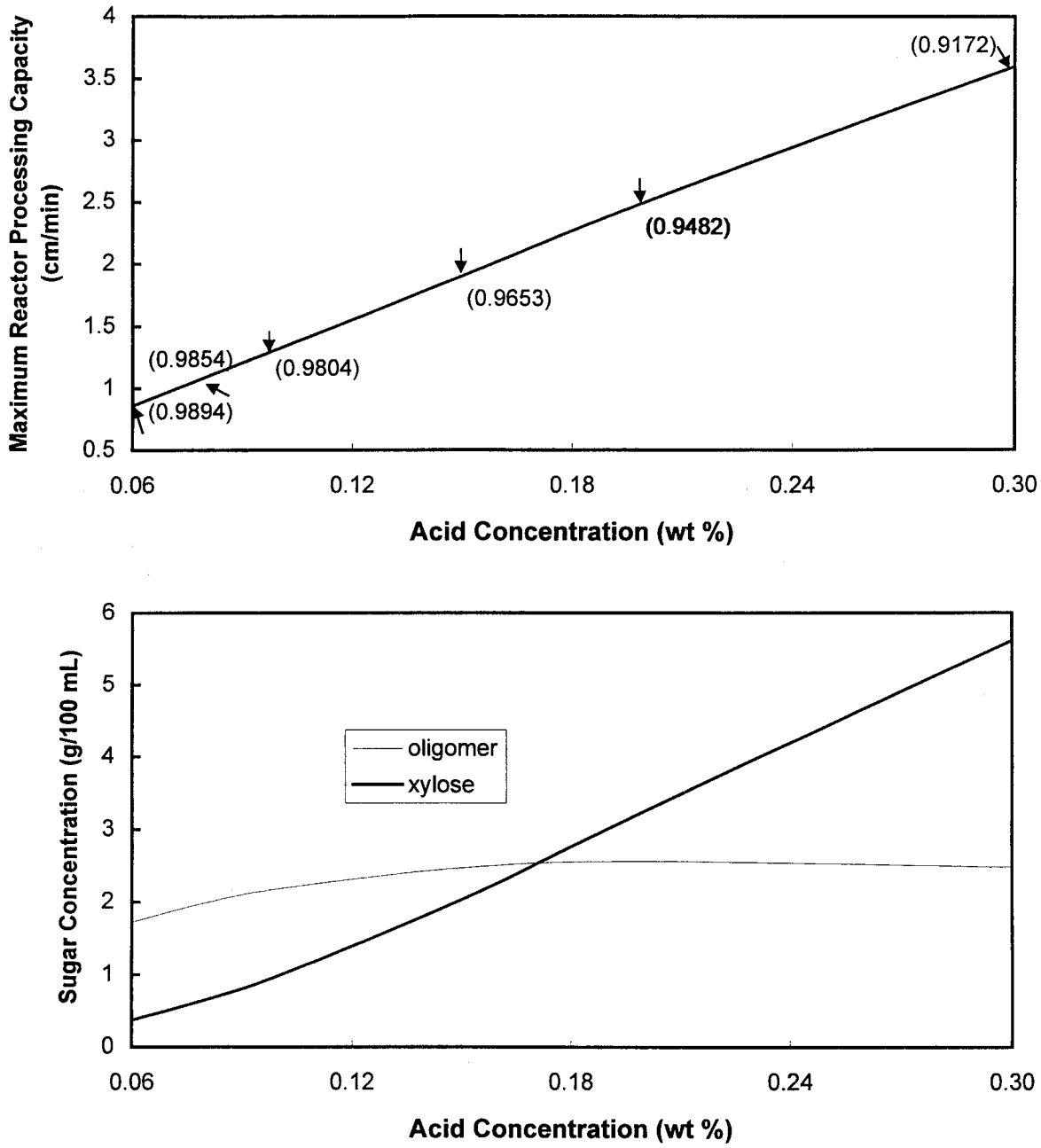


Figure 6. Effect of acid concentration on the hydrolysis of hemicellulose. Assumption: u = 2 cm/min and T =190 C, Peclet no = 20.

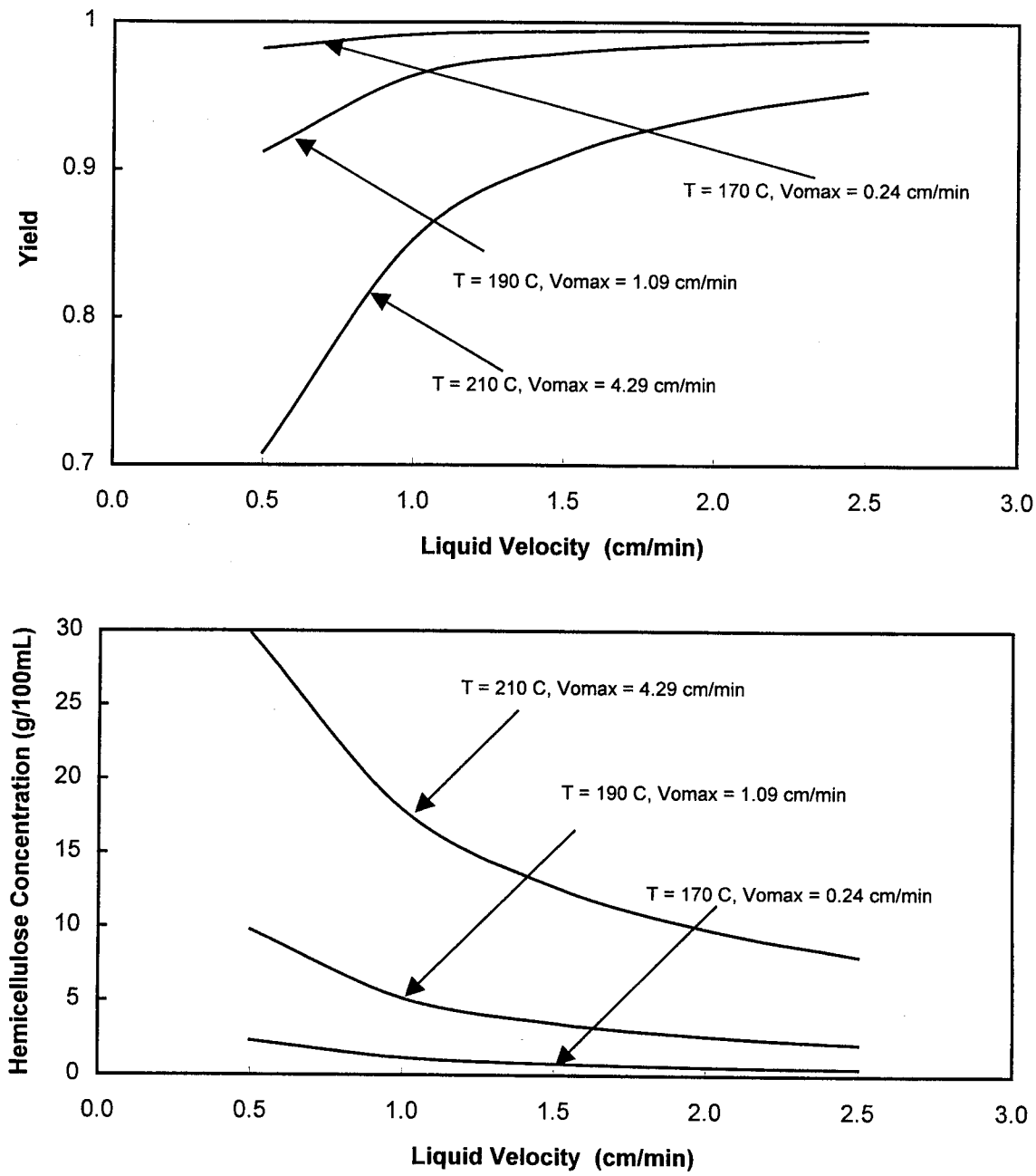


Figure 7. Effect of acid flow velocity on the hydrolysis of hemicellulose at different temperatures. Assumption: acid concentration = 0.08 wt%, Peclet no = 20

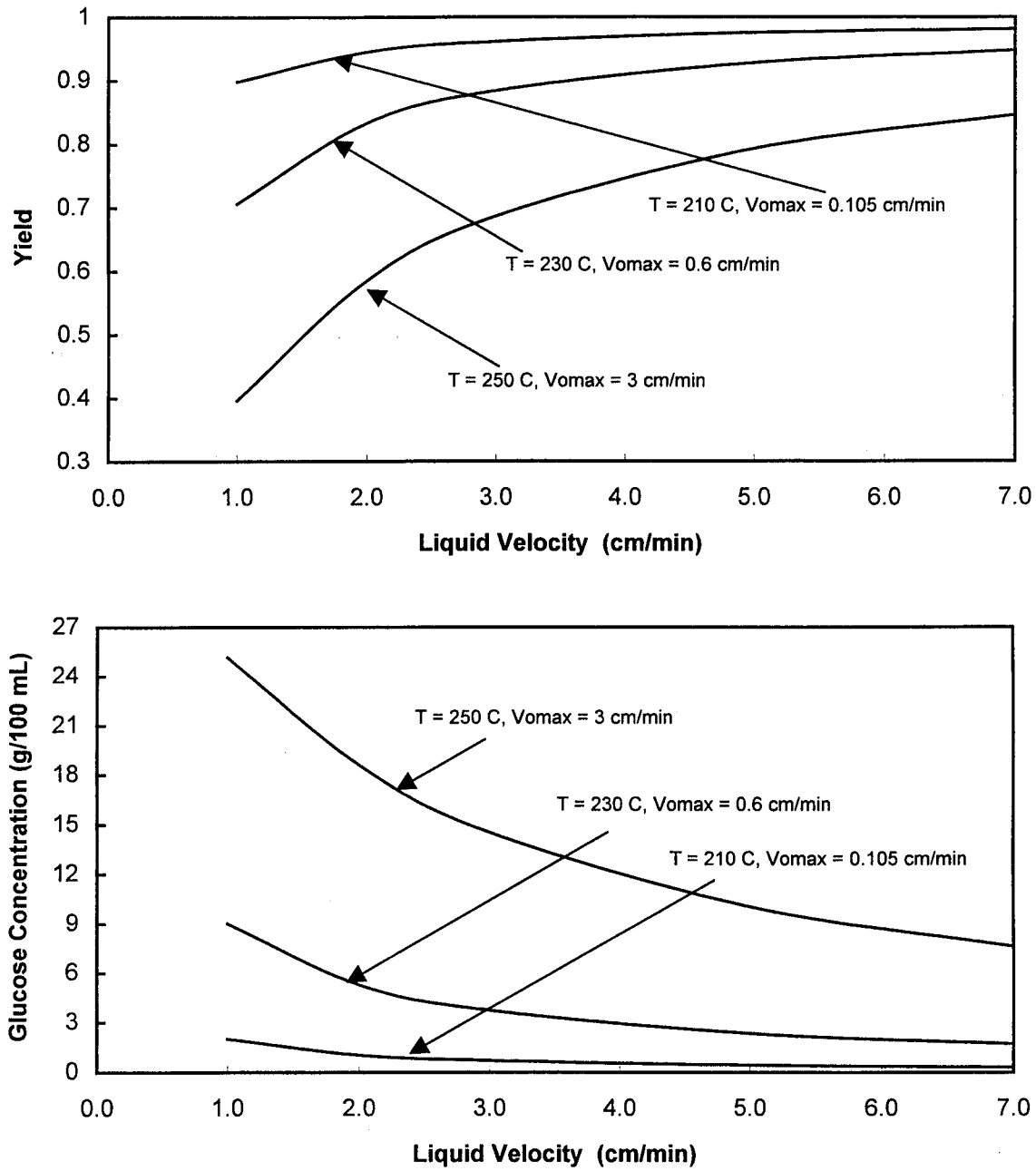
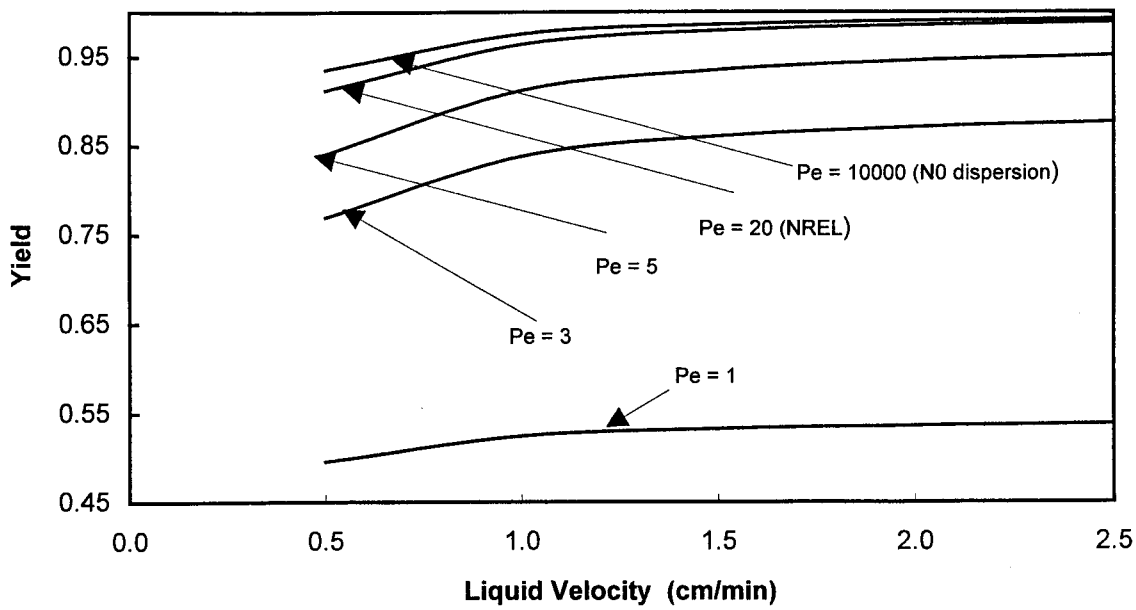


Figure 8. Effect of acid flow velocity on the hydrolysis of cellulose at different temperatures. Assumption: acid concentration = 0.08 wt%, Peclet no = 20



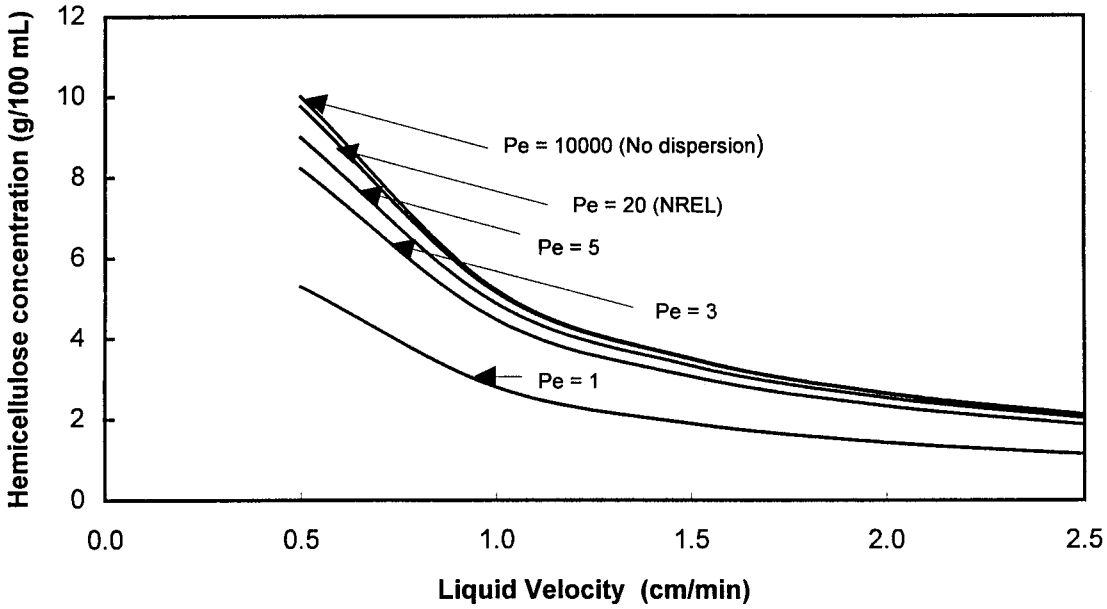


Figure 9. Effect of acid flow velocity on the hydrolysis of hemicellulose at different dispersion levels. Assumption: T = 190 C, Vomax = 1.09 cm/min, acid concentration = 0.08 wt%

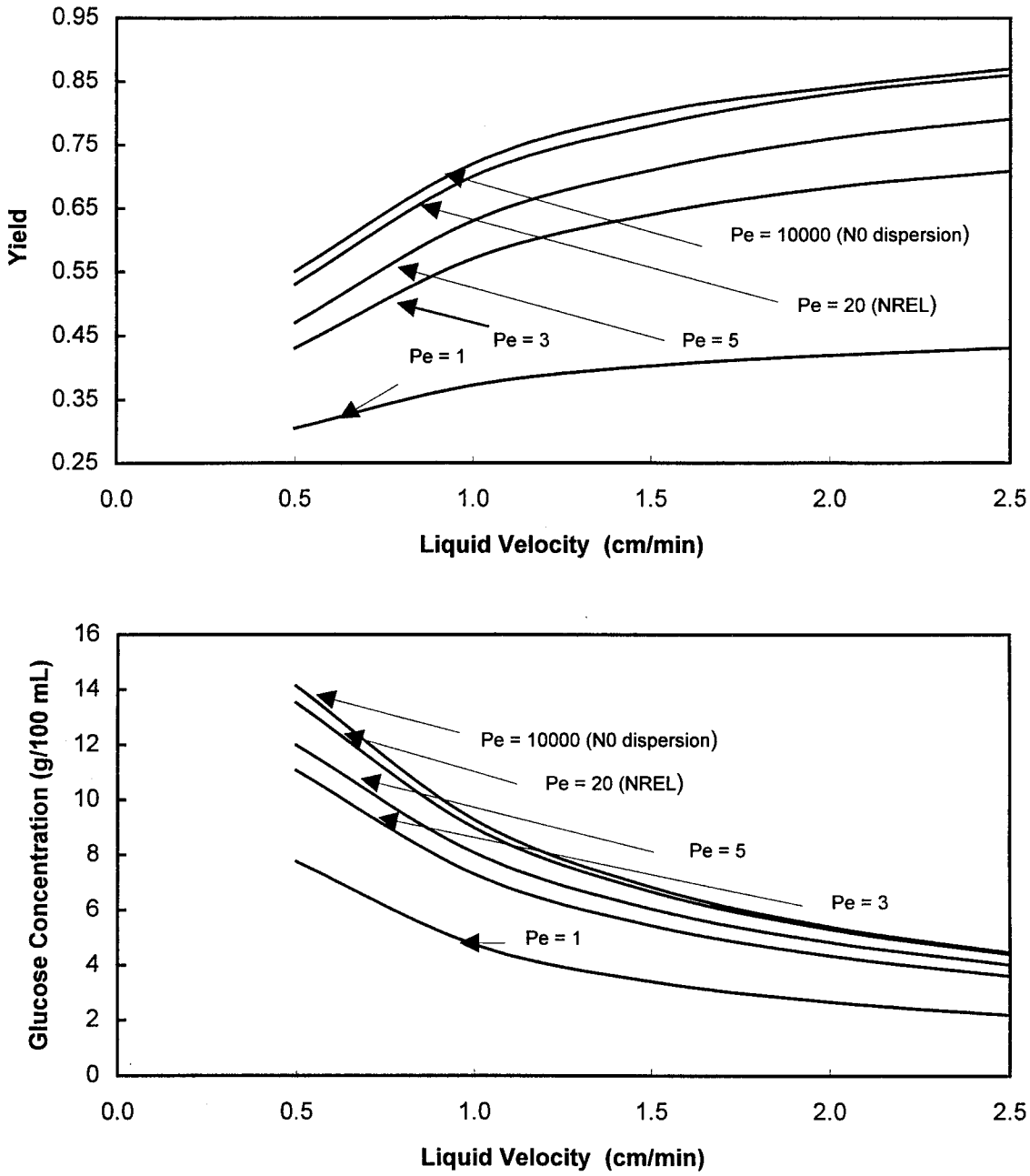


Figure 10. Effect of acid flow velocity on the hydrolysis of cellulose at different dispersion levels. Assumption: T = 230 C, Vomax = 0.6 cm/min, acid concentration = 0.08 wt%

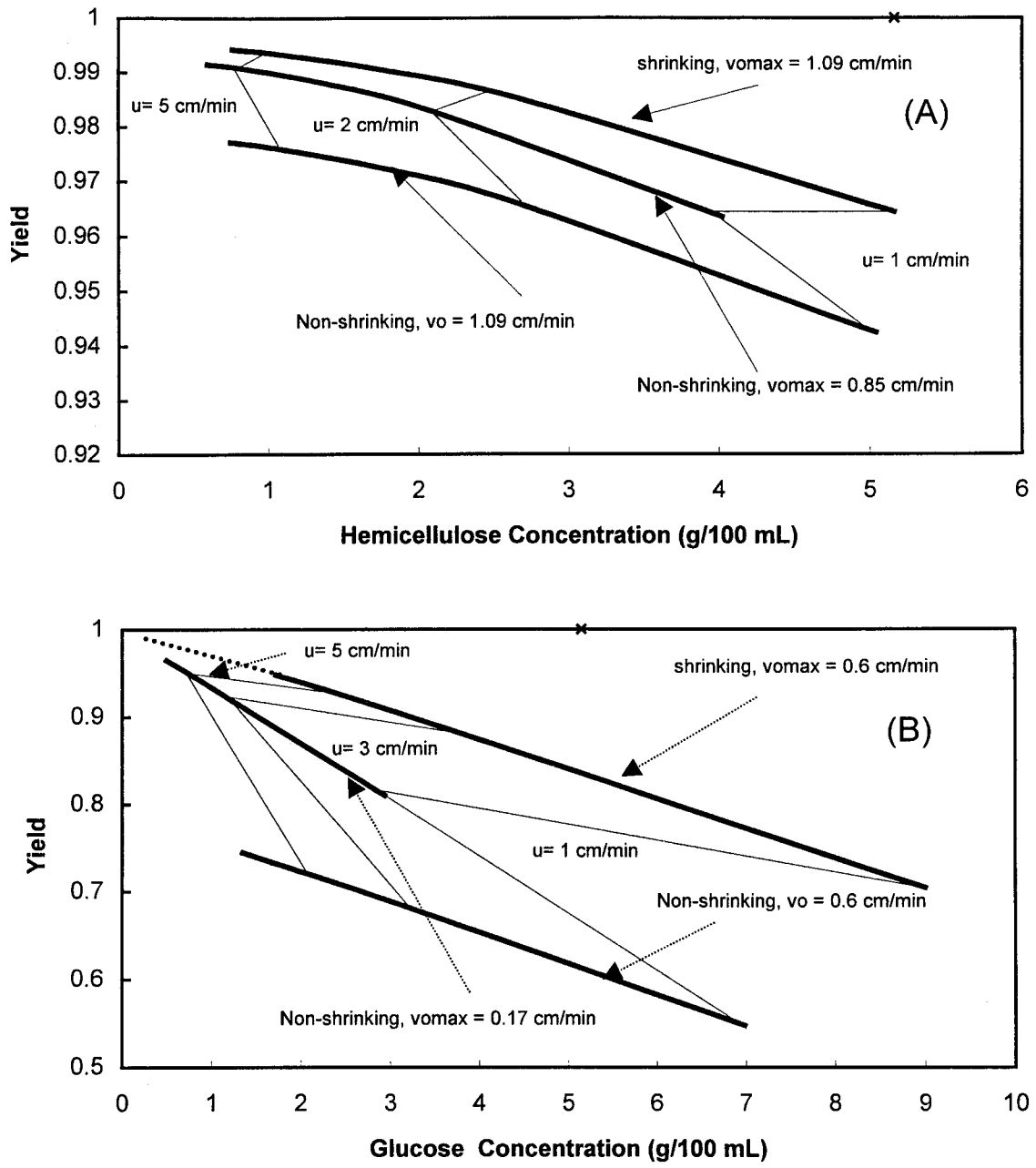


Figure 11. Yield vs. sugar product concentration under shrinking and non-shrinking operation mode. (A) Hemicellulose hydrolysis, (B) Cellulose hydrolysis. Assumptions: acid concentration = 0.08 wt%, Pe = 20, T = 190 C for hemicellulose hydrolysis and T = 230 C for cellulose hydrolysis.

Task 2: Verification of Hydrolysis Kinetics of Cellulose of Yellow Poplar Sawdust using 0.07 wt% Suulfuric Acid

The kinetic investigation was conducted in two separate phases; decomposition of pure glucose, hydrolysis of glucan in Yellow Poplar Sawdust. In the method, the level of glucose was measured for the former, and the remaining glucan for the latter. The glucan hydrolysis was done for conversion up to 60%. The kinetics at higher conversion is left as a future task.

Experiment:

Kinetic experiments on glucan hydrolysis by acid and on glucose decomposition were conducted in a 6-inch nickel tube reactors. The reactor were sealed at both ends with Swagelok caps. The nickel tube was obtained from Salem Tube, Inc., Greenville, PA. The supplier's test report indicates that the purity of the nickel is >99.5%.

Two oil baths were used for temperature control of reactor tubes. One of the two oil baths was set at 250 C to reduce the pre-heating time. The reactor tubes were first placed in this bath and moved to another bath set at desired reaction temperature. Preheating time ranged between 45 to 70 seconds depending on the reaction temperature chosen. Four levels of temperature were applied: 205C, 215C, 225C and 235C. At the end of the reaction, the reactors was quickly chilled with ice-water to terminate the reaction.

Glucose concentration of 6 g/L was used for all glucose decomposition experiments. For the cellulose hydrolysis experiments, dilute-acid pretreated yellow poplar was used as the substrate. Pretreatment conditions were, 7mM sulfuric acid, 150C, 15 min, 195C, 15min. The pretreated substrate contained 69.5 wt% glucan and 28.0 wt% klason lignin on a dry basis. The pretreated yellow poplar was stored in the cool room under wet condition (without water

washing). Moisture content was determined to be 84%. For all kinetic experiments, a sulfuric acid solution of 7 mM (0.0684 wt%) was used. The reactor was packed with 0.9 g substrate and 9 mL acid solution to achieve a solid to liquid ratio of 1:10. A reaction time of less than 7 minutes was chosen for glucose decomposition experiments whereas reaction time up to 30 minutes were applied for cellulose hydrolysis. After reaction, solids remaining were collected and washed. The overall weight remaining and glucan content were determined. The glucan content remaining after the reaction was used as input data in determination kinetic parameters.

Data Analysis:

A first order reaction model was used to determine kinetic parameters. Linear regression was employed to determine the first order rate constants (Equation ln(CAO/Ca) = K*t). The oligomers of glucose was not found in the hydrolyzates of cellulose. Since only one level of acid concentration was used in the kinetic study, the rate constant equation was simplified to K=ko*exp(-E/RT).

The experimental results are shown in Figures 1 & 2. From these data, k values at different temperature were determined by linear regression. Then using these K values, E and ko were determined from the Arrhenius plot. The activation energy(E) and the frequency factor (ko) thus determined for the respective rate constants are as follows. obtained are produced below.

Glucose decomposition:

ko=1.81E+13

E=33.215 kcal/mol

Cellulose hydrolysis:

ko=1.4E+18

E=44.511 kcal/mol

It is duly noted here that the activation energy for hydrolysis is substantially higher than that of sugar decomposition even at high temperature and low acid conditions.

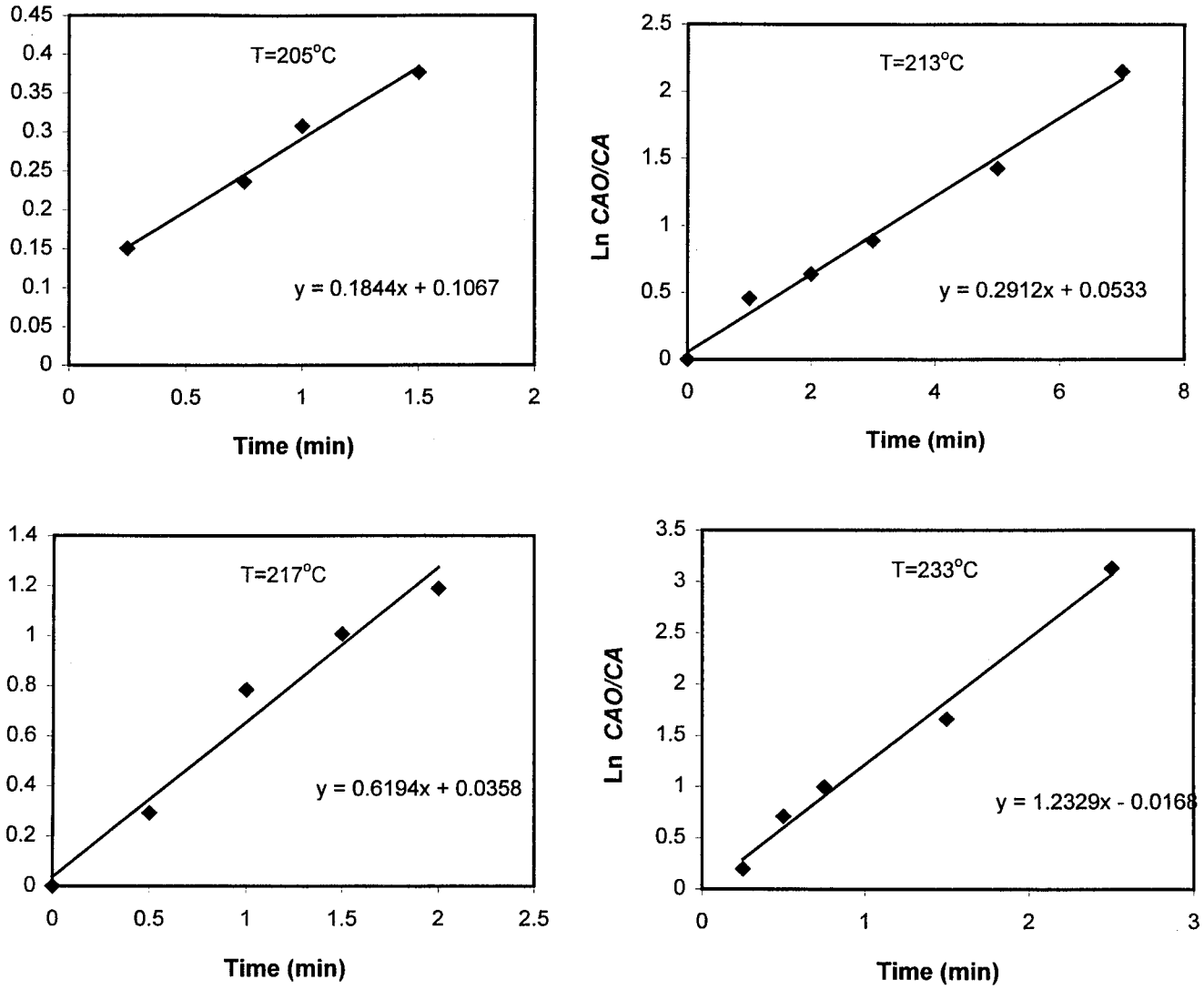


Fig.1 Batch kinetic data for glucose decomposition, 0.0686wt% sulfuric acid

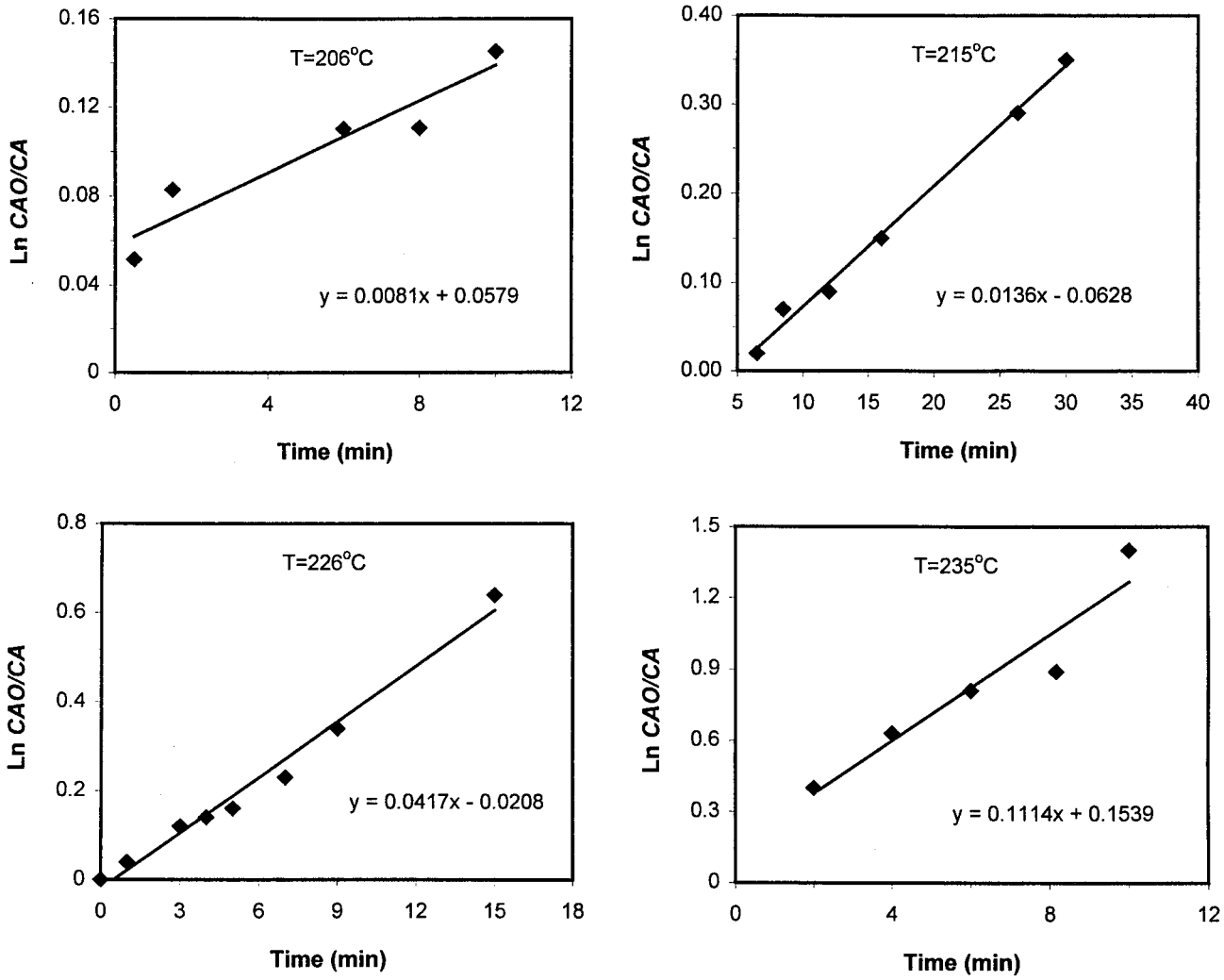


Fig.2 Batch kinetics data for cellulose hydrolysis, 0.0686wt% sulfuric acid
(Measured by remaining cellulose)

Batch data set, cellulose hydrolysis, 7 mM sulfuric acid

T=206.4C	T(K)	1/T*1000	-lnk	kc			
206.4	479.55	2.085288	-4.815891	0.0081	ko =	1.4E+18	
215.5	488.65	2.046455	-4.297685	0.0136	E =	44.511	kcal/mol
226.4	499.55	2.001802	-3.153556	0.0427			
235	508.15	1.967923	-2.194628	0.1114			

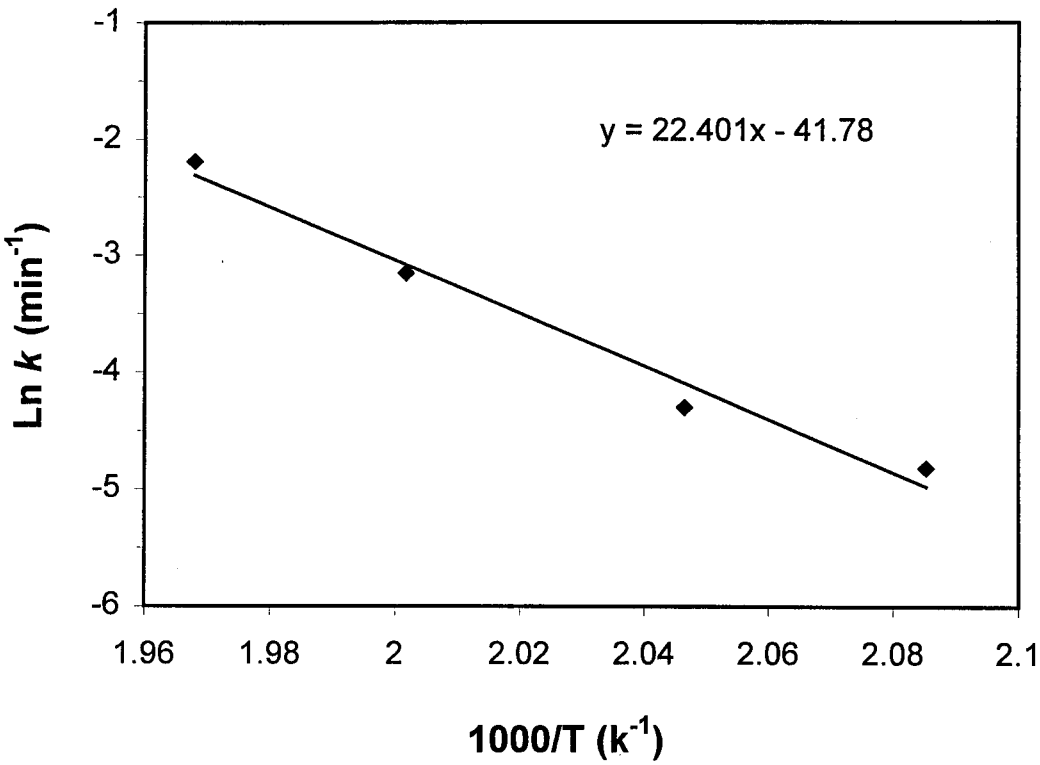


Fig. 3 Arrhenius plot for cellulose hydrolysis, 0.0686wt% sulfuric acid (Substrate: dilute-acid pretreted yellow poplar sawdust)

Batch data set, glucose degradation

T(C)	T(K)	1000/T	lnk	k			
205	478.15	2.091394	-1.69119	0.1843	ko =	1.81E+13	
213	486.15	2.056978	-1.233745	0.2912	E =	33.215	kcal/mol
217	490.15	2.040192	-0.486296	0.6149			
233	506.15	1.975699	0.209369	1.2329			

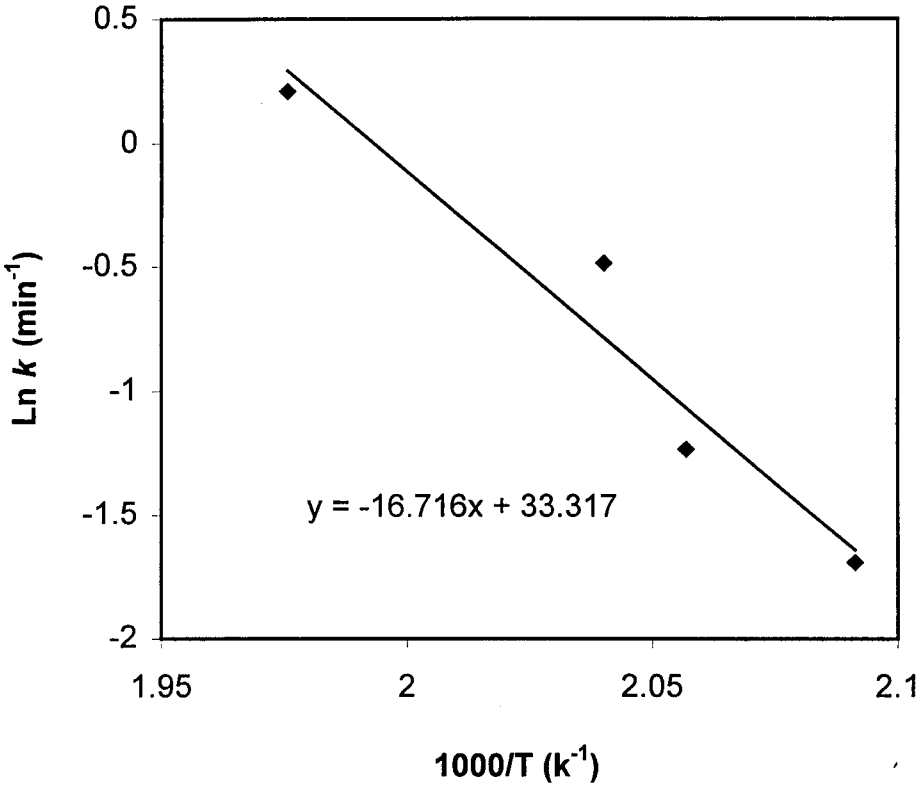


Fig.4 Arrhenius plot for glucose decomposition, 0.0686wt% sulfuric acid

Task 3: Preliminary Investigation on Thermal/Oxidative Cracking of Lignin Generated from Total Hydrolysis process

Oxidative Degradation of Lignin by Hydrogen Peroxide

Lignins are complex amorphous phenolic polymers. Their composition in various biomass species ranges from 18% to 33% by weight. The aromatic complex nature of lignins suggests that they can be converted into low-molecular-weight compounds, potential precursors for fuels or chemicals. Various approaches have been taken for this purpose including hydrotreating and pyrolysis. Mild hydrodeoxygenation and dealkylation can give a mixture of substituted phenolic compounds and hydrocarbons as main products. The phenolics can be converted to methyl or ethyl aryl ethers (MAE or EAE). The mixture of alkyl aryl ethers and hydrocarbons may become a low-vapor-pressure octane enhancer that is fully compatible with gasoline.

Chemically, lignin is very reactive. It is easily oxidizable and can undergo a variety of acid- and based- catalyzed hydrolysis reactions. Oxidized by alkaline nitrobenzene, lignin provides a high yield of vanillin. The yield of 20 to 28% vanillin is typical for spruce lignin. Various degradation products from the permanganate oxidation of spruce lignin have been identified. Hemipinic acid and the biphenyls, diphenyl ethers, and the benzene polycarboxylic acids are among that group detected along with the main product of veratric isohemipinic, and metahemipinic acids. Hydrogen peroxide is a very strong oxidation reagent which has been successfully used in waste water treatment to remove organic material. The advantage of using hydrogen peroxide as the oxidation reagent is that there is no residuals left after the reaction and it is quite safe to handle. The oxidative degradation of lignin degradation using hydrogen peroxide is an interesting concept that deserves further investigation. There has been a substantial research work conducted on utilizing hydrogen peroxide in treatment of solid wastes such as waste carpet

remnants and waste plastics by a research team in the Chemical Engineering Department in Auburn University. With the aid of this group, we have carried out a series of preliminary investigation on oxidative degradation of lignin by aqueous hydrogen peroxide near critical temperature of water.

Experimental

Materials:

A commercial grade Kraft lignin (brand name of Indulin) was supplied by Westvaco, Charleston, SC. Hydrogen peroxide purchased as 30% solution from Fisher was used after dilution to 10% and 5%. Methylene Chloride was used as the extraction reagent for GC/MS analysis.

Batch Reaction:

Batch reactions were carried out using tubing bomb reactors (SS-316, 3/4", 11 cm^3 in volume) capped at both ends with Swagelok screw caps. The reaction was carried out in a temperature controlled electric oven (Thermolyne 314). A 250 rpm agitation was applied to the reactor assembly during the reaction for mixing of reactor content. For a given reaction temperature, the amount of liquid (water) to put into the reactor was calculated from steam table pressure data. At the completion of reaction, the reactor was quenched in tab water. The reactor content was brought into contact with methylene chloride for extraction. The resulting liquid sample samples (methylene chloride phase) were analyzed by GC/MS.

Reaction Conditions:

Four batch reactions have been carried out at various conditions. The detailed reaction conditions are shown in Table 1. Tests 1 and 2 are at supercritical condition of water. After the reaction the lignin powder (solids) have totally disappeared. The remaining liquid showed light tan color. Gaseous products were also formed from the reaction. It is quite obvious that all of the lignin has reacted, perhaps over-reacted. The tests made here represent only sketchy spot checks. Further experiments would be needed to

identify proper reaction conditions in terms of including temperature, reaction time, and reactant ratio (lignin/ H_2O_2).

Table 1: Reaction Conditions

Reaction Condition	Test 1	Test 2	Test 3	Test 4
Temperature ^{0}C	400	400	350	300
Pressure (bar)	350	350	250	100
Reaction Time	30 min	15 min	30 min	30 min
Lignin (g)	0.0536	0.0550	0.0850	0.0813
H_2O_2 (g)	4.29 (10%)	4.281(10%)	6.924 (5%)	8.175 (5%)

Analysis:

Methylene Chloride was used as extraction solvent for the products. About 1:1 volume of methylene chloride was added for extraction of reaction products. The analysis of this extraction sample was done by GC/MS. A sample GC chromatogram is attached for each test.

For **test 1**, which was carried out at the highest temperature (400 ^{0}C) and with longest reaction time (30 min), GC chromatogram showed that very little non-volatile products in the solvent. **Test 2** was carried out also at 400 ^{0}C , but with 15 minutes of reaction time. Two major were shown at 213 and 227 respectively. By mass spectrograph analysis, the most possible product name at 213 peak is either $C_5H_7NO_2$ (2,5 - pyrrolidinedione, 1-methyl-) or C7H12O3 is. For the peak at 227, $C_8H_{13}NO_2$ or $C_8H_{18}N_2$ were suggested by a computer-based finger printing, but the possibility of confirmation were quite low in both cases (59%). It is also noted that the concentration of former is much higher than the latter. A few other peaks of this run were identified as the products derived form silicon oil used in the screw of the reactor. The silicon oil was not used for tests 3 and 4.

Test 3 was ran at 350 ^{0}C for 30 min. The number of products has sharply increased for this run to more than 20. The computer finger printing suggested that the possible products of this run include: $C_6H_{14}O$ (2,3-dimethyl-1-butanol) at peak 17, C_6H_6O (phenol) at peak 114, $C_5H_7NO_2$ (1-methyl-2,5 - pyrrolidinedione) or $C_7H_{12}O_3$ at peak 198, $C_{14}H_{20}O_2$ at peak 573, $C_{15}H_{16}O$ at peak 830, alkanes such as C_9H_{20} and $C_{12}H_{26}$, and $C_{18}H_{20}$ (2,4-diphenyl-4-methyl-pentene).

Test 4 was ran at 300^{0}C for 30 min. There were much less products in this run that in test 3. The main products are: C_6H_7NO (1-methyl 1H-pyrrole-2-carboxaldehyde), C_8H_{18} (3-Ethyl-2-methyl-pentane) or C_9H_{20} (3,4-dimethyl-heptane), and $C_{15}H_{16}O$ (2,3-dimethyl-1-butanol or 2-methyl-1-pentanol). The full sketch of the products are shown in Table 2.

Table 2. Main Products in the solvent

Experiment No.	Peak at	Possible Elements	Possible Product name
Test 1		No products detected	
Test 2	**213 ***	$C_5H_7NO_2$ or $C_7H_{12}O_3$	(1-methyl-2,5 - pyrrolidinedione) or (1)**
	227	$C_8H_{13}NO_2$ or $C_8H_{18}N_2$	(3-ethyl-1, 3-dimethyl-2, 5-pyrrolidinedione) or (2-propanone, ethyl<1-methylethyl>hydrazone)
Test 3	17	$C_6H_{14}O$	(2,3-dimethyl-1-butanol) or (2-methyl-1-pentanol)
	31	C_9H_{20}	(2,3,5-thrmethyl-hexane) or (4-methyl-octane)
	114 *	C_6H_6O	(phenol)
	198 *	$C_5H_7NO_2$ or $C_7H_{12}O_3$	(1-methyl-2,5 - pyrrolidinedione) or (1)**
	573	$C_{14}H_{20}O_2$	(2,5-cyclohexadiene-1,4-dione,2,6-bis<1,1-dimethylethyl>-)
	837	$C_{18}H_{20}$	(2,4-diphenyl-4-methyl-2<Z>-pentene)
	912	$C_{18}H_{20}$	(2,4-diphenyl-4-methyl-2<E>-pentene)
	951	$C_{18}H_{20}$	(2,4-diphenyl-4-methyl-2<E>-pentene)
	1186	no fit found	no fit found
	1274	$C_{13}H_{28}$	(2,4,6-trimethyl-decane) or (3,7-dimethyle-undecane)
	1355	$C_{13}H_{28}$	(3,7-dimethyle-undecane) or (3,8-dimethyl-undecane)
	1432	$C_{12}H_{26}$	(3,8-dimethyl-undecane) or (2,4,6-trimethyl-dodecane)
	1513	$C_{28}H_{34}O$	(2,4-bis<dimethylbenzyl>-6-T-butylphenol
Test 4	20	$C_6H_{14}O$	(2,3-dimethyl-1-butanol) or (2-methyl-1-pentanol)
	34	C_8H_{18} or C_9H_{20}	(3-Ethyl-2-methyl-pentane) or (3,4-dimethyl-heptane)
	142 *	C_6H_7NO	(1-methyl 1H-pyrrole-2-carboxaldehyde)
	144 *	C_6H_7NO	(1-methyl 1H-pyrrole-2-carboxaldehyde)

* : Major products

(1)** : Full identification unavailable.

Direction of Future Research

The results obtained to this point indicate that the proposed scheme of utilizing hydrogen peroxide as the oxidative lignin degradation reagent is a valid concept that warrants further investigation although the results are sketchy at this point. The following are the main items of investigation we think should be pursued if this research is to be explored.

1. Verification of the mechanisms of the oxidation reaction between lignin (biomass-to-ethanol lignin) and hydrogen peroxide.
2. Expand the reaction conditions in terms of temperature, pressure, reagent ratio, and reaction time and identify the products in liquid and gas phase.
3. Evaluate the reaction performance and efficiency of the process under selected reaction conditions.
4. Evaluate the economic factors for the process.
5. Assimilate a process design and integrate into the biomass-to- ethanol process.

Preparation of Lignin Generated during Total Hydrolysis of Yellow Poplar

In addition to the work described above, a sample quantity of yellow poplar lignin was prepared and sent to Dr. B. Hames of NREL for preliminary test and comparison of properties between this and the one produced from NREL total hydrolysis system.

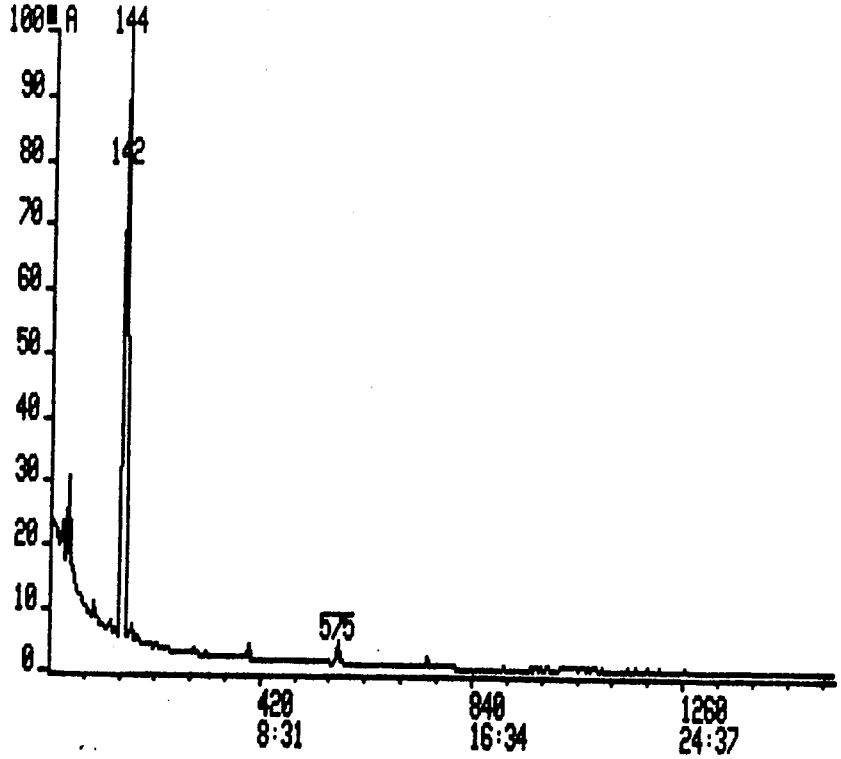
For lignin production, a medium sized perocolation reactor (3"ID x 12"L) was operated in three stages, 174C, 225C, and 235C with 0.07% H_2SO_4, taking one reactor volume fluid at each stage. The reaction conditions were identical to those applied in the NREL total hydrolysis system with one exception that the spring assisted bed compaction is not applied here. The hydrolysates at each stage were collected separately and stored in a refrigerator overnight. The lignin precipitated during this

process was filtered and dried. The quantity of lignin generated during the first stage was less than 0.1 g. The lignin samples sent to NREL were the ones generated in the last two stages.

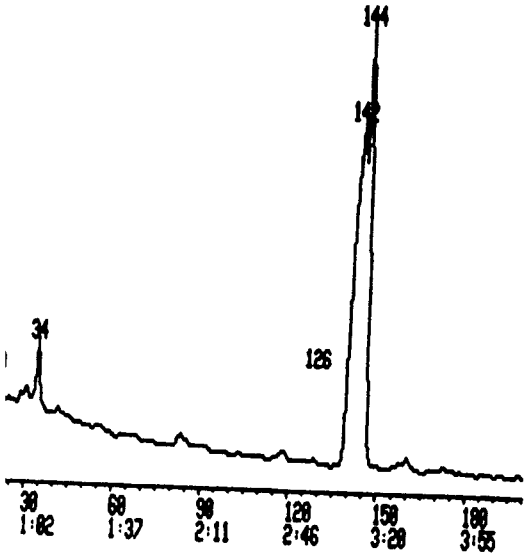
Attachment:

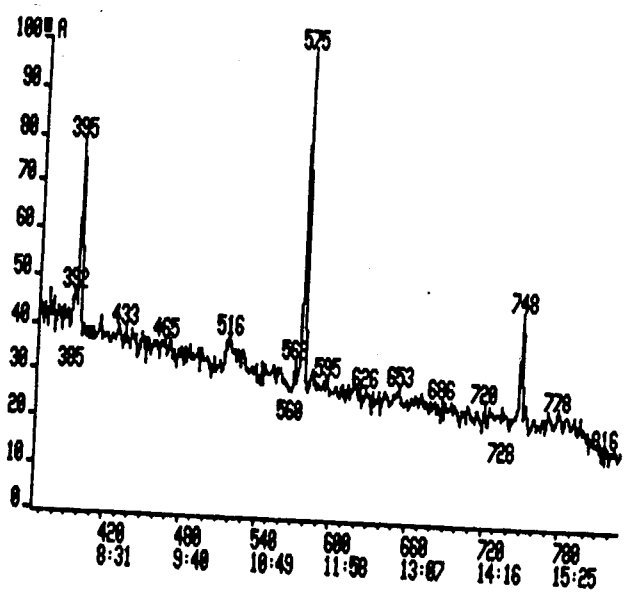
GC Graph

Test 4



(Detail)

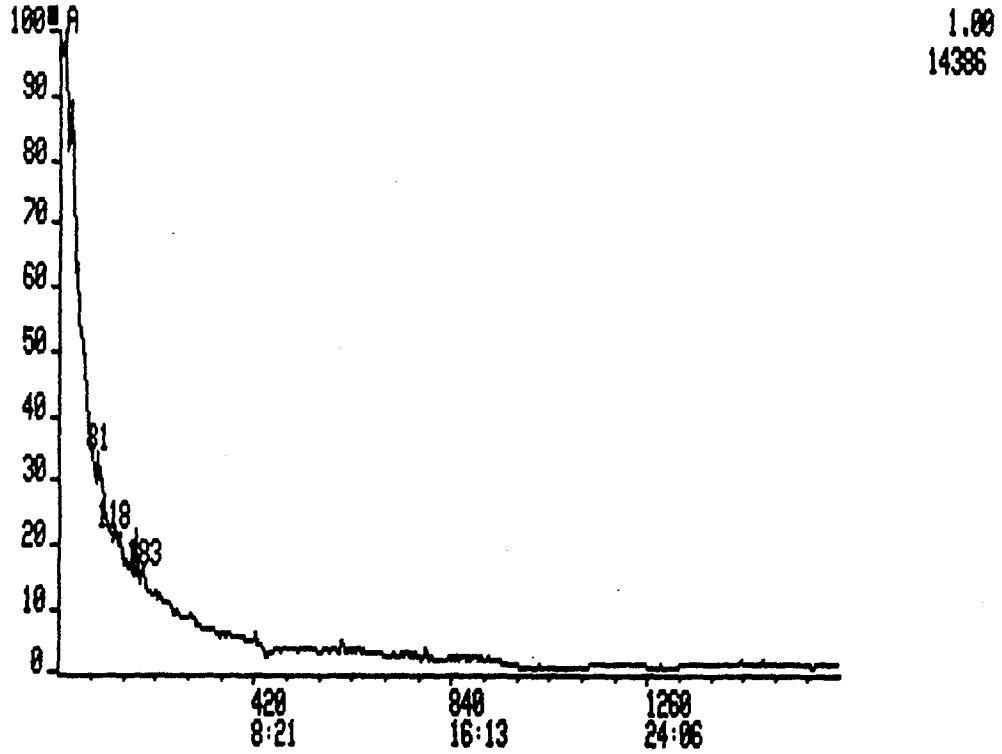




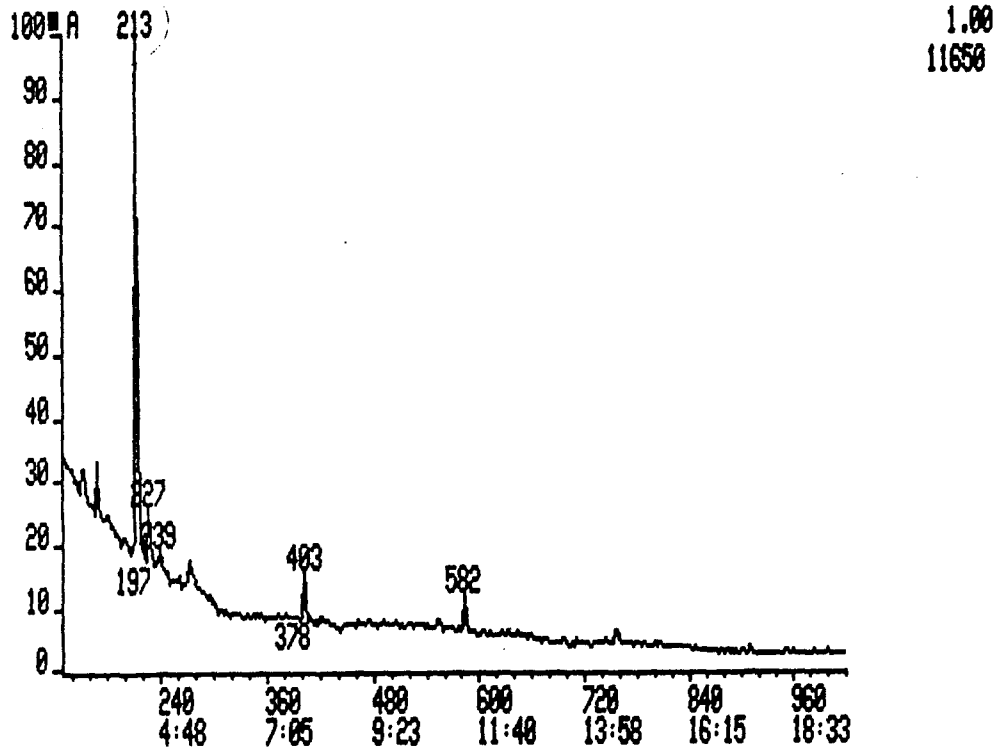
Attachment:

GC Graph

Test 1



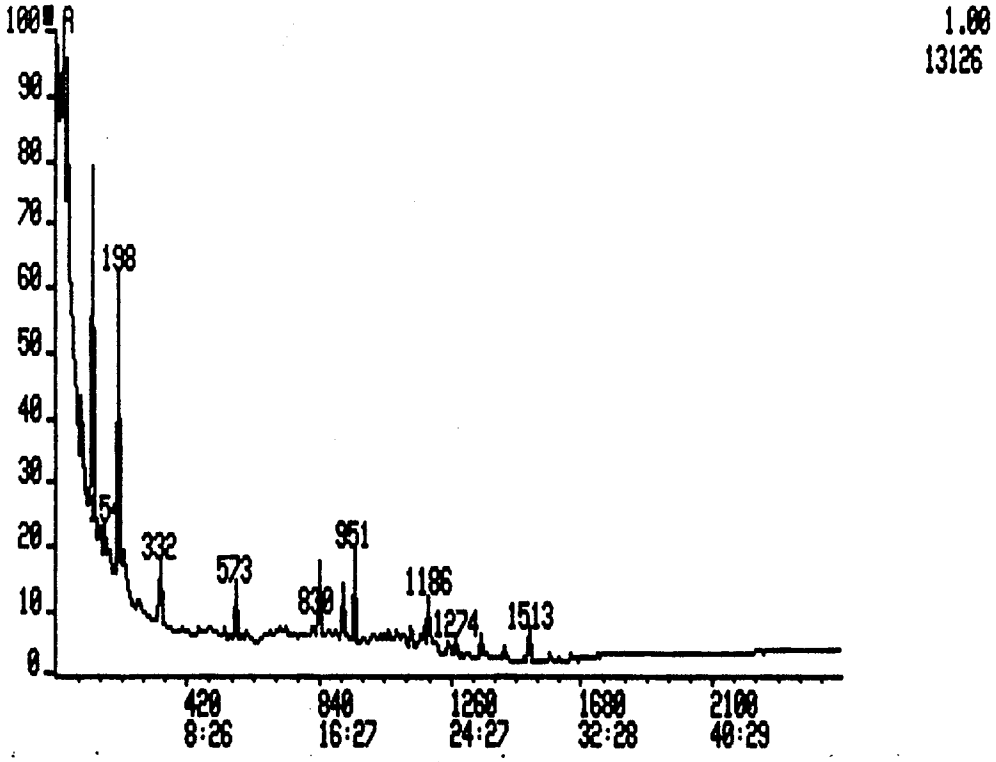
Test 2



Attachment:

GC Graph

Test 3



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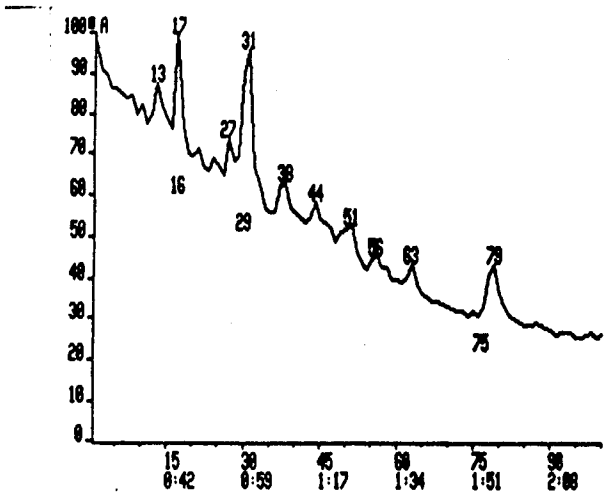

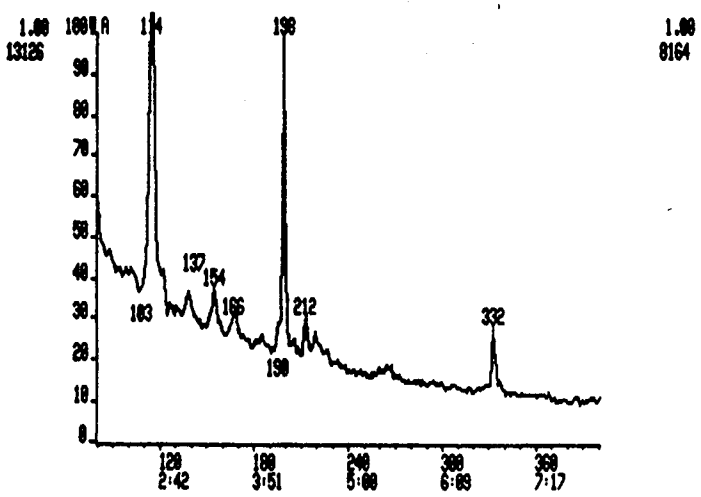

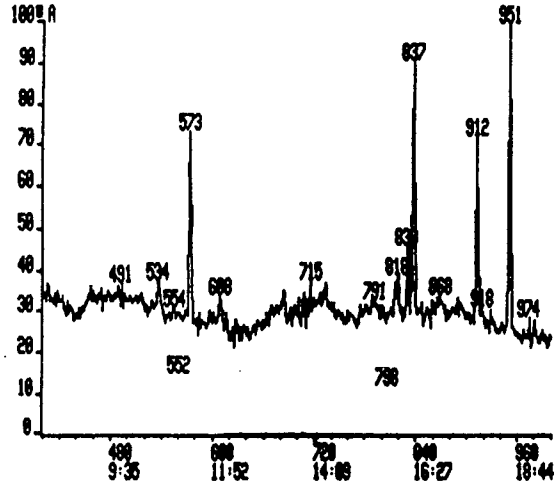

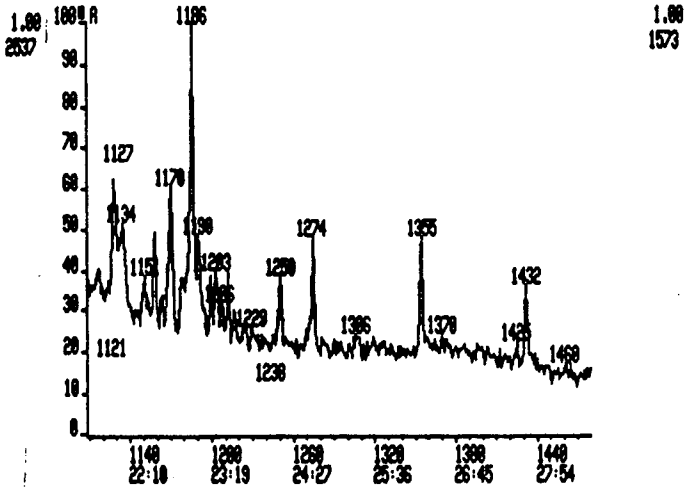

Appendix 1

Fortran Program Source Codes for Modeling of Counter-Current Bed-Shrinking Reactor

Notes:

1. This program has been installed into the NREL PC along with the Microsoft Fortran and tested for actual reactor simulation.

2. This program requires 4 subroutines from IMSL library available from Microsoft Professional Fortran program package and external functions defined within the program.

```
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
     This program calculates xylose yield in countercurrent shrinking and        c
     nonshrinking bed reactor.  The reaction follows pattern:                    c
                K1              k2           k4                                  c
         HC (A)--->Oligomer (B)--->Xylose(C)--->Decomposition                    c
     Since the uniform temperature, the biphasic nature of hemicellulose is      c
     reflected on the overall K, K=F*1+ (1-F)k2                                  c
                                                                                 c
     Process varables: tem, u(liquid velocity: cm/min), vo(solid velocity:cm/min) c
                    acid concentration, g/100 ml.                                c
     Out put data: Z (L/Lo), YA(Ca/Cao), YB(Cb/Cao), YC(Cc/CAo)                  c
     then yield and sugar concentration can be calculated from YB, YC.           c
         Yield=epsilon*(YB+Yc)*omega, here omega =u/vo                           c
                                                                                 c
     when let f=0.0001, the process was forced to be a nonshrinking one          c
                                                                                 c
     Modified date: 03/03/98 by Prashant V Iyer
   c
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
     use          msimsl
     real         tem, ac, vo, u, bee, coef1, coef2
     real         lamd, Cao, omega, epsilon
     real         yield(100), olig(100), xylose(100),qq(100)


                                  SPECIFICATIONS FOR PARAMETERS
     INTEGER     LDYFIN, LDYINI, MXGRID, NEQNS, NINIT
     PARAMETER   (MXGRID=1000, NEQNS=5, NINIT=10, LDYFIN=NEQNS,
    &            LDYINI=NEQNS)
                                  SPECIFICATIONS FOR LOCAL VARIABLES
     INTEGER     I, J, NCUPBC, NFINAL, NLEFT, NOUT
     REAL        ERREST(NEQNS), PISTEP, TFINAL(MXGRID), TINIT(NINIT),
    &            TLEFT, TOL, TRIGHT, YFINAL(LDYFIN,MXGRID),
    &            YINIT(LDYINI,NINIT)
     LOGICAL     LINEAR, PRINT
                                  SPECIFICATIONS FOR INTRINSICS
     INTRINSIC   FLOAT
     REAL        FLOAT
                                  SPECIFICATIONS FOR SUBROUTINES
      EXTERNAL    BVPFD, SSET, UMACH
                                  SPECIFICATIONS FOR FUNCTIONS
     EXTERNAL     FCNBC, FCNEQN, FCNJAC
     REAL         FCNBC, FCNEQN, FCNJAC

                                  Set parameters
     NLEFT  = 2
     NCUPBC = 0.0
     TOL    = .001
     TLEFT  = 0.0
     TRIGHT = 1.0
     PISTEP = 0.0
     PRINT  = .FALSE.
     LINEAR = .FALSE.
                                  Define TINIT
     DO 10  I=1, NINIT
        TINIT(I) = TLEFT + (I-1)*(TRIGHT-TLEFT)/FLOAT(NINIT-1)
  10 CONTINUE
                                  Set YINIT to zero
     DO 20  I=1, NINIT
        CALL SSET (NEQNS, 0.0, YINIT(1,I), 1)
```

```
20 CONTINUE

   call coeff(tem, ac, vo, u, bee, coef1, coef2,alpha3,alpha4,
  &lamd,Cao,omega,epsilon,f)
   Print*, lamd
   open(unit=3,file="run1.dat",status="old")
   write(3,66)
66 format (2X,'Tem',10X,'ac',6x,'vo',6x,'u',8x,'Cao',4x,'epsilon',
  &4x,'f')
   write (*, 77) tem, ac, vo, u, Cao, epsilon, f
77 format(2x,F4.0, 7x, F5.2,3x,f5.1,2x,f5.1,4x,f6.2, 3x, f5.2,
  &5x, f5.2)

   write(*,6)
 6 format (2X,'Tem',10X,'ac',6x,'vo',6x,'u',8x,'Cao',4x,'epsilon',
  &4x,'f')
   write (3, 7) tem, ac, vo, u, Cao, epsilon, f
 7 format(2x,F4.0, 7x, F5.2,3x,f5.1,2x,f5.1,4x,f6.2, 3x, f5.2,
  &5x, f5.2)
   Print*, 'T=',tem, 'ac=',ac, 'vo=', vo, 'u=', v
   print*, Cao, lamd, luo
           solve problem
   CALL BVPFD (FCNEQN, FCNJAC, FCNBC, FCNEQN, FCNBC, NEQNS, NLEFT,
  &            NCUPBC, TLEFT, TRIGHT, PISTEP, TOL, NINIT, TINIT,
  &            YINIT, LDYINI, LINEAR, PRINT, MXGRID, NFINAL,
  &            TFINAL, YFINAL, LDYFIN, ERREST)

       Calculation and Printing results

   write(*,5)
 5 format (2X, 'I', 5X, 'Z', 6X, 'YA',6X, 'YB',6X, 'YC', 5X, 'Yield',
  & 3X, 'Oligomer', 3X, 'Xylose', 3X, 'v/vo')
   write(3,55)
55 format (2X, 'I', 5X, 'Z', 6X, 'YA',6X, 'YB',6X, 'YC', 5X, 'Yield',
  & 3X, 'Oligomer', 3X, 'Xylose', 3X, 'v/vo')

   do 555 m=1, nfinal
   yield(m)=(yfinal(2,m)+yfinal(4,m))*omega*epsilon
   olig(m)=Cao*yfinal(2,m)
   xylose(m)=Cao*yfinal(4,m)
   qq(m)=(lamd-1.)/(lamd-yfinal(1, m))
   write(*,44) m, tfinal(m), yfinal(1,m), yfinal(2,m), yfinal(4,m),
  & yield(m), olig(m), xylose(m), qq(m)

   write(3,44) m, tfinal(m), yfinal(1,m), yfinal(2,m), yfinal(4,m),
  & yield(m), olig(m), xylose(m), qq(m)
44 format (2X, I1, 2X, F5.2, 2X, F6.3,2X, F6.3,2X, F6.3, 2X, F7.4,
  & 2X, F7.3, 2X, F7.3, 3X, F6.3)

555 continue
   print*, yfinal(1,1)
   end


   END


   SUBROUTINE FCNEQN (NEQNS, T, Y, P, DYDX)
                                SPECIFICATIONS FOR ARGUMENTS
```

```
      INTEGER     NEQNS
      REAL        T, P, Y(NEQNS), DYDX(NEQNS)
C                                 SPECIFICATIONS FOR INTRINSICS


      real     tem, ac, vo,u, bee, coef1, coef2,alpha3,alpha4
      real     lamd, Cao, omega, epsilon
      call coeff(tem, ac, vo, u, bee, coef1, coef2,alpha3,alpha4,
     &lamd,Cao,omega,epsilon,f)

C                                 Define ODE
      DYDX(1) = coef1*(Y(1)**3-2.0*lamd*Y(1)**2+lamd**2*Y(1))
      DYDX(2) = Y(3)
      DYDX(3) = coef2*(Y(3)-bee/epsilon*Y(1)+bee*alpha3*y(2))
      DYDX(4) = Y(5)
      DYDX(5) = coef2*(Y(5)-bee*alpha3*Y(2)+bee*alpha4*Y(4))

      RETURN
      END

      SUBROUTINE FCNJAC (NEQNS, T, Y, P, DYPDY)
C                                 SPECIFICATIONS FOR ARGUMENTS
      INTEGER     NEQNS
      REAL        T, P, Y(NEQNS), DYPDY(NEQNS,NEQNS)

      real     tem, ac, vo,u, bee, coef1, coef2,alpha3,alpha4
      real     lamd, Cao, omega, epsilon
      call     coeff(tem, ac, vo, u, bee, coef1, coef2,alpha3,alpha4,
     &lamd,Cao,omega,epsilon,f)

C                              Define d(DYDX)/dY

      DYPDY(1,1) = coef1*(3.0*Y(1)**2-4.0*lamd*Y(1)+lamd**2)
      DYPDY(1,2) = 0.0
      DYPDY(1,3) = 0.0
      DYPDY(1,4) = 0.0
      DYPDY(1,5) = 0.0
      DYPDY(2,1) = 0.0
      DYPDY(2,2) = 0.0
      DYPDY(2,3) = 1.0
      DYPDY(2,4) = 0.0
      DYPDY(2,5) = 0.0
      DYPDY(3,1) = -coef2*bee/epsilon
      DYPDY(3,2) = coef2*bee*alpha3
      DYPDY(3,3) = coef2
      DYPDY(3,4) = 0.0
      DYPDY(3,5) = 0.0
      DYPDY(4,1) = 0.0
      DYPDY(4,2) = 0.0
      DYPDY(4,3) = 0.0
      DYPDY(4,4) = 0.0
      DYPDY(4,5) = 1.0
      DYPDY(5,1) = 0.0
      DYPDY(5,2) = -coef2*bee*alpha3
      DYPDY(5,3) = 0.0
      DYPDY(5,4) = coef2*bee*alpha4
      DYPDY(5,5) = coef2

      RETURN
      END
```

```
      SUBROUTINE FCNBC (NEQNS, YLEFT, YRIGHT, P, F)
C                                   SPECIFICATIONS FOR ARGUMENTS
      INTEGER     NEQNS
      REAL        P, YLEFT(NEQNS), YRIGHT(NEQNS), F(NEQNS)
C                                   Define boundary conditions
      F(1) = YLEFT(2)
      F(2) = YLEFT(4)
      F(3) = YRIGHT(1) - 1.0
      F(4) = YRIGHT(3)
      F(5) = YRIGHT(5)

      RETURN
      END

      subroutine  coeff(tem, ac, vo,u,bee, coef1, coef2,alpha3,alpha4,
     &lamd,Cao,omega,epsilon,f)
      real     tem, ac ,u, vo, L, f, Ho, F1,luo, Cao
      real     omega,epsilon alpha3, alpha4, peclet
      real     bee, coef1, coef2, coef3, lamd
      real     K1, an(4), k0(4), e(4), k(4), kk(4)
C
c         Input Initial data
c     unit: vo, u =cm/min; luo=g/ml, HC =g/100g, Cao=g/100mL
          Tem =190
          ac  =0.08

          u   =2.
          vo  =1.6
c     Print*, tem, ac, u,vo
          f   =1.82

          epsilon=0.8

          L   =15.24
          Ho  =19.63
          F1  =0.7
          luo =1.0

      Cao     =luo*Ho*(1.- epsilon)
      omega   =u/vo
      lamd    =(1.-epsilon)*luo*100/(f*Cao)
      peclet  =10000


C             Input kinetic data
C
          an(1) = 1.0
          an(2) = 0.5
          an(3) = 1.5
          an(4) = 0.8
          k0(1) = 1.458E15
          k0(2) = 1.3E14
          k0(3) = 6.372E10
          k0(4) = 1.618E12
          e(1) = 30.9E3
          e(2) = 30.0E3
          e(3) = 21.0E3
          e(4) = 27.5E3
```

```
C             Calculate kk(i) = k*a**an(i)
C
      do 888 i=1, 4
          k(i) = k0(i)*exp(-e(i)/1.987/(tem + 273.15))
          kk(i) = ac**an(i)*k(i)
c         bee(i) = kk(i)*L/u
  888 continue
c         print*, ac, an
c         print*, bee
C
          K1  =F1*kk(1)+(1.-F1)*kk(2)
          bee = k1*L/u
          alpha3  = kk(3)/K1
          alpha4  = kk(4)/K1

          coef1 = bee*omega/lamd/(lamd-1.)
          coef2= peclet


c     print*, c
      return
      end
```

```
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
c     This program calculates glucose yield in countercurrent shrinking and         c
c     nonshrinking bed reactor.
c                                                                                   c
c     Process variables: tem, u(liquid velocity: cm/min), vo(solid velocity:cm/min) c
c                        acid concentration, g/100 ml.                              c
c
c
c                                                                                   c
c     when let f=0.0001, the process was forced to be a nonshrinking one            c
c                                                                                   c
c     Modified date: 03/03/98 by Prashant V Iyer

cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      use          msimsl
      real         tem, ac, vo, u, bee, coef1, coef2
      real         lamd, Cao, omega, epsilon
      real         yield(100), glucose(100), qq(100)


C                                  SPECIFICATIONS FOR PARAMETERS
      INTEGER    LDYFIN, LDYINI, MXGRID, NEQNS, NINIT
      PARAMETER  (MXGRID=1000, NEQNS=5, NINIT=10, LDYFIN=NEQNS,
     &           LDYINI=NEQNS)
C                                  SPECIFICATIONS FOR LOCAL VARIABLES
      INTEGER    I, J, NCUPBC, NFINAL, NLEFT, NOUT
      REAL       ERREST(NEQNS), PISTEP, TFINAL(MXGRID), TINIT(NINIT),
     &           TLEFT, TOL, TRIGHT, YFINAL(LDYFIN,MXGRID),
     &           YINIT(LDYINI,NINIT)
      LOGICAL    LINEAR, PRINT
C                                  SPECIFICATIONS FOR INTRINSICS
      INTRINSIC  FLOAT
      REAL       FLOAT
C                                  SPECIFICATIONS FOR SUBROUTINES
c      EXTERNAL   BVPFD, SSET, UMACH
C                                  SPECIFICATIONS FOR FUNCTIONS
      EXTERNAL    FCNBC, FCNEQN, FCNJAC
      REAL        FCNBC, FCNEQN, FCNJAC

C                                  Set parameters
      NLEFT  = 2
      NCUPBC = 0.0
      TOL    = .001
      TLEFT  = 0.0
      TRIGHT = 1.0
      PISTEP = 0.0
      PRINT  = .FALSE.
      LINEAR = .FALSE.
C                                  Define TINIT
      DO 10  I=1, NINIT
         TINIT(I) = TLEFT + (I-1)*(TRIGHT-TLEFT)/FLOAT(NINIT-1)
   10 CONTINUE
C                                  Set YINIT to zero
      DO 20  I=1, NINIT
         CALL SSET (NEQNS, 0.0, YINIT(1,I), 1)
   20 CONTINUE


      call coeff(tem, ac, vo, u, bee, coef1, coef2,alpha3,alpha4,
     &lamd,Cao,omega,epsilon,f)
```

```
      Print*, lamd
      open(unit=3,file="run2.dat",status="old")
      write(3,66)
   66 format (2X,'Tem',10X,'ac',6x,'vo',6x,'u',8x,'Cao',4x,'epsilon',
     &4x,'f')
      write (*, 77) tem, ac, vo, u, Cao, epsilon, f
   77 format(2x,F4.0, 7x, F5.2,3x,f5.1,2x,f5.1,4x,f6.2, 3x, f5.2,
     &5x, f5.2)

      write(*,6)
    6 format (2X,'Tem',10X,'ac',6x,'vo',6x,'u',8x,'Cao',4x,'epsilon',
     &4x,'f')
      write (3, 7) tem, ac, vo, u, Cao, epsilon, f
    7 format(2x,F4.0, 7x, F5.2,3x,f5.1,2x,f5.1,4x,f6.2, 3x, f5.2,
     &5x, f5.2)
      Print*, 'T=',tem, 'ac=',ac, 'vo=', vo, 'u=', v
      print*, Cao, lamd, luo
              solve problem
      CALL BVPFD (FCNEQN, FCNJAC, FCNBC, FCNEQN, FCNBC, NEQNS, NLEFT,
     &            NCUPBC, TLEFT, TRIGHT, PISTEP, TOL, NINIT, TINIT,
     &            YINIT, LDYINI, LINEAR, PRINT, MXGRID, NFINAL,
     &            TFINAL, YFINAL, LDYFIN, ERREST)

          Calculation and Printing results

      write(*,5)
    5 format (2X, 'I', 5X, 'Z', 6X, 'YA',6X, 'YG',6X, 'YD', 5X, 'Yield',
     & 3X, 'glucose', 3X, 'glucose', 3X, 'v/vo')
      write(3,55)
   55 format (2X, 'I', 5X, 'Z', 6X, 'YA',6X, 'YG',6X, 'YD', 5X, 'Yield',
     & 3X, 'glucose', 3X, 'glucose', 3X, 'v/vo')

      do 555 m=1, nfinal
      yield(m)=yfinal(2,m)*omega*epsilon
      glucose(m)=Cao*yfinal(2,m)
      glucose(m)=Cao*yfinal(2,m)
      qq(m)=(lamd-1.)/(lamd-yfinal(1, m))
      write(*,44) m, tfinal(m), yfinal(1,m), yfinal(2,m), yfinal(4,m),
     & yield(m), glucose(m), glucose(m), qq(m)

      write(3,44) m, tfinal(m), yfinal(1,m), yfinal(2,m), yfinal(4,m),
     & yield(m), glucose(m), glucose(m), qq(m)
   44 format (2X, I1, 2X, F5.2, 2X, F6.3,2X, F6.3,2X, F6.3, 2X, F7.4,
     & 2X, F7.3, 2X, F7.3, 3X, F6.3)

  555 continue
      print*, yfinal(1,1)

      END


      SUBROUTINE FCNEQN (NEQNS, T, Y, P, DYDX)
                                  SPECIFICATIONS FOR ARGUMENTS
      INTEGER     NEQNS
      REAL        T, P, Y(NEQNS), DYDX(NEQNS)
                                  SPECIFICATIONS FOR INTRINSICS

      real     tem, ac, vo,u, bee, coef1, coef2,alpha3,alpha4
      real     lamd, Cao, omega, epsilon
      call coeff(tem, ac, vo, u, bee, coef1, coef2,alpha3,alpha4,
```

```
     &lamd,Cao,omega,epsilon,f)

C                                   Define ODE
      DYDX(1) = coef1*(Y(1)**3-2.0*lamd*Y(1)**2+lamd**2*Y(1))
      DYDX(2) = Y(3)
      DYDX(3) = coef2*(Y(3)-bee/epsilon*Y(1)+bee*alpha3*y(2))
      DYDX(4) = Y(5)
      DYDX(5) = coef2*(Y(5)-bee*alpha3*Y(2)+bee*alpha4*Y(4))

      RETURN
      END

      SUBROUTINE FCNJAC (NEQNS, T, Y, P, DYPDY)
C                                   SPECIFICATIONS FOR ARGUMENTS
      INTEGER    NEQNS
      REAL       T, P, Y(NEQNS), DYPDY(NEQNS,NEQNS)

      real    tem, ac, vo,u, bee, coef1, coef2,alpha3,alpha4
      real    lamd, Cao, omega, epsilon
      call    coeff(tem, ac, vo, u, bee, coef1, coef2,alpha3,alpha4,
     &lamd,Cao,omega,epsilon,f)

C                              Define d(DYDX)/dY

      DYPDY(1,1) = coef1*(3.0*Y(1)**2-4.0*lamd*Y(1)+lamd**2)
      DYPDY(1,2) = 0.0
      DYPDY(1,3) = 0.0
      DYPDY(1,4) = 0.0
      DYPDY(1,5) = 0.0
      DYPDY(2,1) = 0.0
      DYPDY(2,2) = 0.0
      DYPDY(2,3) = 1.0
      DYPDY(2,4) = 0.0
      DYPDY(2,5) = 0.0
      DYPDY(3,1) = -coef2*bee/epsilon
      DYPDY(3,2) = coef2*bee*alpha3
      DYPDY(3,3) = coef2
      DYPDY(3,4) = 0.0
      DYPDY(3,5) = 0.0
      DYPDY(4,1) = 0.0
      DYPDY(4,2) = 0.0
      DYPDY(4,3) = 0.0
      DYPDY(4,4) = 0.0
      DYPDY(4,5) = 1.0
      DYPDY(5,1) = 0.0
      DYPDY(5,2) = -coef2*bee*alpha3
      DYPDY(5,3) = 0.0
      DYPDY(5,4) = coef2*bee*alpha4
      DYPDY(5,5) = coef2

      RETURN
      END


      SUBROUTINE FCNBC (NEQNS, YLEFT, YRIGHT, P, F)
C                                   SPECIFICATIONS FOR ARGUMENTS
      INTEGER    NEQNS
      REAL       P, YLEFT(NEQNS), YRIGHT(NEQNS), F(NEQNS)
C                                   Define boundary conditions
      F(1) = YLEFT(2)
```

```
      F(2) = YLEFT(4)
      F(3) = YRIGHT(1) - 1.0
      F(4) = YRIGHT(3)
      F(5) = YRIGHT(5)

      RETURN
      END

      subroutine  coeff(tem, ac, vo,u,bee, coef1, coef2,alpha3,alpha4,
     &lamd,Cao,omega,epsilon,f)
      real    tem, ac ,u, vo, L, f, Ho, F1,luo, Cao
      real    omega,epsilon alpha3, alpha4, peclet
      real    bee, coef1, coef2, coef3, lamd
      real    K1, an(4), k0(4), e(4), k(4), kk(4)

          Input Initial data
      unit: vo, u =cm/min; luo=g/ml, HC =g/100g, Cao=g/100mL
          Tem =225
          ac  =0.08

          u   = 3.5
          vo  =0.505
      Print*, tem, ac, u,vo
          f   =0.001

          epsilon=0.84

          L   =15.24
          Ho  =85.
          F1  =0.65
          luo =1.0

      Cao     =luo*Ho*(1.- epsilon)
      omega   =u/vo
      lamd    =(1.-epsilon)*luo*100/(f*Cao)
      peclet  = 6.25


              Input kinetic data

          an(1) = 1.
          an(2) = 1.
          an(3) = 1.
          an(4) = 1.0
          k0(1) = 5.86E17
          k0(2) = 5.86E17
          k0(3) = 1.81E13
          k0(4) = 0.
          e(1) = 44.511E3
          e(2) = 44.511E3
          e(3) = 33.215E3
          e(4) = 33.215E3

              Calculate kk(i) = k*a**an(i)

      do 888 i=1, 4
          k(i) = k0(i)*exp(-e(i)/1.987/(tem + 273.15))
          kk(i) = 1**an(i)*k(i)
          bee(i) = kk(i)*L/u
  888 continue
```

```
    print*, ac, an
    print*, bee

    K1  =F1*kk(1)+(1.-F1)*kk(2)
    bee = k1*L/u
    alpha3  = kk(3)/K1
    alpha4  = kk(4)/K1

    coef1 = bee*omega/lamd/(lamd-1.)
    coef2= peclet


return
end
```

Appendix 2

List of Papers Published or Submitted for Publication

Full or partial financial support from NREL is acknowledged for the following papers.

Published-

1. Rongfu Chen and Y. Y. Lee, "Shrinking -Bed Model for Percolation Process Applied to Dilute-Acid Pretreatment/Hydrolysis of Cellulosic Biomass", Applied Biochem. & Biotechnol., Vol. 70-72, 37-50, 1998

2. Zhangwen Wu and Y. Y. Lee, "Non-isothermal Simultaneous Saccharification and Fermentation for Direct Conversion of Lignocellulosic Biomass to Ethanol", Applied Biochem. & Biotechnol, 70-72, 479-492, 1998

3. Zhangwen Wu and Y. Y. Lee, "Effect of Ethanol on Enzymatic Hydrolysis of Cellulose", Biotechnology Letters,Vol.9, No.10, 977-979, 1997,

***Submitted-**

1. Zhangwen Wu, Y. Y. Lee, and R. W. Torget, "Modeling of Countercurrent Continual Shrinking-Bed Reactor System Applied to theDilute-Acid Hydrolysis of Lignocellulosic Biomass", Submitted for publication in Biotechnol Bioresource Technology

2. Prashant Iyer and Y. Y. Lee, "Simultaneous Fermentation and Extractive Fermentation of Lignocellulosic Materials into Lactic Acid in Two-Zone Fermenter-Extractor System", Submitted for publication in Applied Biochem. & Biotechnol Technology,

*Abstracts are attached.

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14. ABSTRACT *(Maximum 200 Words)*

Following up on previous work, subcontractor investigated three aspects of using NREL “pretreatment” technology for total hydrolysis (cellulose as well as hemicellulose) of biomass. Whereas historic hydrolysis of biomass used either dilute acid or concentrated acid technology for hydrolysis of both hemicellulose and cellulose, NREL has been pursuing very dilute acid hydrolysis of hemicellulose followed by enzymatic hydrolysis of cellulose. NREL’s countercurrent shrinking-bed reactor design for hemicellulose hydrolysis (pretreatment) has, however, shown promise for total hydrolysis. For the first task, subcontractor developed a mathematical model of the countercurrent shrinking bed reactor operation and, using yellow poplar sawdust as a feedstock, analyzed the effect of: initial solid feeding rate, temperature, acid concentration, acid flow rate, Peclet number (a measure of backmixing in liquid flow), and bed shrinking. For the second task, subcontractor used laboratory trials, with yellow poplar sawdust and 0.07 wt% sulfuric acid at various temperatures, to verify the hydrolysis of cellulose to glucose (desired) and decomposition of glucose (undesired) and determine appropriate parameters for use in kinetic models. Unlike cellulose and hemicellulose, lignins, the third major component of biomass, are not carbohydrates that can be broken down into component sugars. They are, however, aromatic complex amorphous phenolic polymers that can likely be converted into low-molecular weight compounds suitable for production of fuels and chemicals. Oxidative degradation is one pathway for such conversion and hydrogen peroxide would be an attractive reagent for this, as it would leave no residuals. For the third task, subcontractor reacted lignin with hydrogen peroxide under various conditions and analyzed the resulting product mix.

15. SUBJECT TERMS
biofuels; ethanol; fuels; chemicals; pretreatment; shrinking bed; feedstock; biomass; cellulose; hemicellulose; lignin; hydrolysis

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